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DEVELOPMENT OF A CHEMICAL KINETIC MECHANISM FOR THE U.S. EPA REGIONAL OXIDANT MODEL

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A new generalized mechanism for use in EPA's Regional Oxidant Model has been developed. The mechanism is based on the carbon-bond concept in which organics are grouped according to the type of carbon bonding that is found in the various classes of organics. The mechanism treats biogenic as well as anthropogenic hydrocarbons. The mechanism was tested against multi-day chamber data collected by the University of California, Riverside and against isoprene/NO_x data obtained in the outdoor chamber facility of the University of North Carolina. In addition to a description of the mechanism, guidance is also given on how emission data should be partitioned into the various organic groupings that are used in the mechanism.

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ABSTRACT

A new chemical kinetics mechanism for modeling regional-scale formation of photochemical oxidant has been developed. The mechanism was tested by comparing computer simulations of smog chamber experiments with extensive smog chamber data. The mechanism, called the Expanded Carbon-Bond Mechanism for Regional Oxidant (CBM-XR), is a hybrid of explicit chemistry, surrogate approximations, and lumped generalized chemistry. Explicit chemistry is used to describe the reactions of the inorganic species, the carbonyls, ethene, isoprene, toluene, and m-xylene. The carbon-bond lumped structure approach is used to treat the reactions of paraffin groups and the carbon double bonds of 1-olefins. Surrogate approximations are used to describe (1) the behavior of internal olefins, which are simulated as a mixture of aldehydes and ketones; (2) monoalkylated aromatics, which are assumed to react like toluene; (3) highly substituted aromatics, which are assumed to react like m-xylene; and (4) the higher aldehydes, which are assumed to react like acetaldehyde.

The CBM-XR actually is the Extended Carbon-Bond Mechanism (CBM-X), developed for urban oxidant chemistry; isoprene chemistry has been added, and the validation base has been extended to include the successful simulation of multiday smog chamber and isoprene experiments. Therefore, the extensive testing performed on the CBM-X applies to the regional version as well. This testing involved individual sets of smog chamber experiments that treated only the compounds associated with the organic parts of the CBM-X such as formaldehyde, acetaldehyde, and ethene. In addition to the CBM-XR, a version of somewhat reduced size called the CBM-RR has also been prepared. This version essentially produces the same simulation results as does the CBM-XR. The CBM-XR contains 170 reactions with 78 species, and the reduced version has 115 reactions using 47 species.

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SECTION 1

INTRODUCTION

The United States Environmental Protection Agency (EPA) is currently developing an air quality simulation model to describe the transport, dispersion, and transformation of photochemical oxidants on a regional scale (Lamb, 1982). Systems Applications, Inc., under contract to the EPA, developed a chemical kinetic mechanism for use in the EPA Regional Oxidant Model (ROM). The development, testing, and use of this mechanism are the subjects of this report.

BACKGROUND

The EPA has sponsored an ongoing coordinated research program focusing on oxidant formation in the troposphere. An integral part of this program is the study of atmospheric chemistry, which involves (1) atmospheric monitoring programs, (2) smog chamber tests, (3) examination of the chemical kinetics of key reactions, and (4) kinetic mechanism development.

A chemical kinetic mechanism comprises a set of chemical reactions and rate constants. Each mechanism represents all of the chemistry considered relevant to a given situation. A chemical kinetic mechanism is a codification of the chemical knowledge of an oxidant-formation event (e.g., a propylene/NO_x smog chamber experiment) and can also be used in a computer model to simulate the same oxidant event. In many instances, the extent of agreement between the computer simulation and observed data is indicative of the state of knowledge represented by the kinetic mechanism. Lack of agreement can arise from a number of factors:

Incomplete reaction set

Inaccurate rate constants

Inappropriate mechanism condensation techniques

Poorly defined "chamber effects"

Inaccurate initial condition measurements

Inaccurate observations

Inadequate computer integration schemes

During the course of the EPA research program, many of these uncertainties have been greatly reduced, and several kinetic mechanisms have been developed that provide close agreement between computer model results and smog chamber data. While the majority of such mechanisms are designed to describe the chemistry of individual organic compounds such as propene or isoprene (Killus and Whitten, 1984a), mechanisms designed for use in atmospheric models must account for the vast number of organics known to exist in the troposphere. This wide application requires the condensation of atmospheric mechanisms for the following reasons:

Current knowledge does not include the detailed chemistry of every organic observed in the atmosphere. Hence, some generalizations must be made regarding species type (olefin, paraffin, etc.) and their atmospheric chemistries.

No computer code exists that can treat the chemistry of the thousands of reactions that occur in the atmosphere.

Some atmospheric models have such detailed treatments of meteorology dispersion, deposition, emissions, and visibility that the chemical kinetic computer code must be limited to treatment of only a small number of chemical reactions.

In many atmospheric applications, the data available to run the model are not detailed enough to justify a kinetic mechanism for more than a few organic species; however, an atmospheric model requires some details regarding speciation of emissions, boundary air, and initial pollutants.

The sensitivity of the atmospheric chemistry for certain types of organics may be similar, and some organics may play a dominant role because of their frequent high concentrations. Hence, condensation may be appropriate in such cases to account for the combined effects of reactivity, typical concentration levels, and special chemical pathways. For example, the chemistry and reactivity of many paraffins are typically quite similar on a per-carbon basis, and the paraffins are generally fairly low in reactivity. Therefore, a single condensed reaction scheme for paraffins may be appropriate since a more detailed treatment might not produce a significant increase in the accuracy of the overall model. On the other hand, it may be appropriate to single out such organics as ethene and toluene in a chemical mechanism because they are often found in significant concentrations, are quite reactive, and have unique atmospheric behavior.

Not all atmospheric models require the same level of condensation. For example, the Empirical Kinetics Modeling Approach (EKMA), which uses a simple, single moving-box type of trajectory model can handle a much larger kinetic mechanism than can existing photochemical grid models. Models such as the ROM under development at EPA are intended for large state-of-the-art computers using the latest designs in computer coding (Lamb, 1982). Hence, the ROM can use a more detailed kinetic scheme than that used in previous grid models such as the Urban Airshed Model (Reynolds et al., 1979). Furthermore, models such as the ROM may require some special chemistry features not previously required in single-day urban models, e.g. careful attention to nighttime chemistry and the chemistry of multiday events. A regional model must also address the chemistry of rural environments in which natural organics such as terpenes can play a significant role.

APPROACH

The mechanism developed in the present study is an extension of one developed simultaneously for use in future versions of EKMA. The extensions consist of an isoprene chemistry subset that is appropriate for rural atmospheres, and further validation tests to insure that the chemistry reliably simulates multiday episodes. The principal mechanism is called the expanded Carbon-Bond Mechanism (CBM-X) and is a hybrid of explicit chemistry, surrogate approximations, and lumped/generalized chemistry designed to simulate the broad features of urban smog chemistry. The development of the CBM-X is described in detail in Whitten, Killus, and Johnson (1985).

The explicit chemistry that forms the inorganic and carbonyl mechanism (ICRS) that is the core of the CBM-X conforms to current literature review studies and has been extensively validated in simple organic/NO_x systems. The explicit and generalized chemical submodels of the CBM-X reflect our current understanding of the oxidation photochemistry of complex hydrocarbons. Each type of chemistry used has been carefully chosen to match the simulation sensitivity, analytical input needs, and state-of-knowledge requirements for an urban photochemical smog mechanism.

Because the CBM-X has been designed for models utilizing simple dispersion algorithms (e.g., EKMA-type models), little effort was made to utilize condensation techniques to reduce computer requirements. Where condensation techniques have been utilized, the goal has been to obtain a realistic balance between analytical inputs, the state of knowledge, typical concentrations of the species concerned, and the expected sensitivity of the overall computer simulations.

The CBM-X mechanism has successfully simulated a new series of auto exhaust and synthetic auto exhaust experiments that use a variety of conditions. These experiments were performed in the outdoor dual chamber facility of the University of North Carolina, which is a well-characterized chamber with extensive analytical capabilities. The variety of conditions used for these experiments included two automobiles, four fuels, several driving cycles, and different methods of sample preparation.

The extended form of the CBM-X is called the CBM-XR; it contains 170 reactions that treat the interactions of 78 species. After this mechanism was developed and tested, it was condensed to a level suitable for use in the ROM. The condensed version of the CBM-XR is called the CBM-RR; it contains 115 reactions and 47 species. Only 11 primary precursors are required to exercise either of these mechanisms in most atmospheric applications: two NO_x species (NO and NO_2), two carbonyl species (formaldehyde and higher aldehydes), two olefinic species (ethylene and the 1-olefins or equivalents), two aromatic species (toluene and m-xylene or equivalents), alkyl carbon atoms (paraffins or paraffinic substituents), carbon monoxide, and isoprene. Other primary precursors such as acetone, higher ketones, glyoxal, methylglyoxal, benzaldehyde, phenols, nitrous acid, hydrogen peroxide, dinitrogen pentoxide, and methyl nitrite, can also be used. This last group has been included because they are intermediate products of the primary precursors and because, under some circumstances, they can also be considered primary species.

The mechanisms described in this report (the CBM-XR and CBM-RR) represent an extension of the urban oxidant CBM-X mechanism in the sense that the new mechanisms contain a subset of reactions to treat the natural hydrocarbon species isoprene. The validation tests of these mechanisms were also extended to include simulations of isoprene/NO_x smog chamber data and of a special set of multiday outdoor smog chamber experiments designed to assess the ability of the mechanisms to accurately predict regional scales.

The development and formulation of the CBM-XR is presented in Section 2. The evaluation of the CBM-XR with experimental data from two smog chambers is presented in Section 3. The reduction of the CBM-XR to a smaller number of chemical species and reaction steps (CBM-RR) for inclusion in the ROM is discussed in Section 4. Concluding remarks are presented in Section 5. Appendix A contains a discussion of CBM-X formulations. Appendixes B and C contain simulation results for the UNC isoprene and outdoor experiments, respectively.

SECTION 2

DEVELOPMENT AND FORMULATION OF THE CBM-XR

INTRODUCTION

The expanded Carbon-Bond Mechanism (CBM-XR) developed in this study and in Whitten, Killus and Johnson (1985) has a hierarchical structure. Its "core," i.e, the basis of the hierarchy, consists of a set of inorganic reactions plus the reactions of the carbonyl species that are central to most photooxidation systems. This "core" reaction set is called the Inorganic and Carbonyl Reaction Set (ICRS) and is the basis of all of our mechanism development studies (Whitten, 1983). The details of the ICRS are described in Whitten, Killus and Johnson (1985); reactions in this core set are the first 79 reactions in Table 1. Reactions 80-146 of the CBM-XR are made up of various organic reaction subsets that describe either specific hydrocarbons (namely ethene, toluene, and m-xylene) important in urban atmospheres or a condensed form of the chemistry of other hydrocarbons (or hydrocarbon structures) also considered important in urban atmospheres. The hydrocarbon components of the CBM-XR are also described in detail by Whitten, Killus, and Johnson (1985). Reactions 147-170 of the CBM-XR describe the chemistry of isoprene. A description of this special organic reaction subset is given at the end of this section.

Table 2 presents additional information needed to derive photolytic rate constants for implementation of the mechanism. Tables 3 through 8 list and define all the species contained in the CBM-XR. Appendix A provides a table that can be used to apportion emission data among the various organic groupings contained in the CBM-XR.

For the most part, the scheme used to represent the hydrocarbon components of the CBM-XR employes the lumped structure method used in the Carbon-Bond Mechanism as first introduced by Whitten et al. (1980). This scheme is based on the treatment of organic molecules as groups of independent atoms, which react according to their local bonding structure. The species treated mechanistically are the carbon atoms of similar structure rather than the organic molecules themselves.

TABLE 1. The expanded Carbon-Bond Mechanism for regional oxidant (CBM-XR).

	REACTIONS^a		RATE CONSTANTS^b	ACTIVATE ENERGY (K)^c
1	NO_2	$= NO + O$	vary	
2	$O + O_2 + M$	$= O_3 + M$	0.0000222	-690.
3	$O_3 + NO$	$= NO_2$	26.6	1430.
4	$O + NO_2$	$= NO$	13800.0	
5	$O + NO_2 + M$	$= NO_3 + M$	0.00232	-600.
6	$O + NO + M$	$= NO_2 + M$	0.00312	-411.
7	$NO_2 + O_3$	$= NO_3$	0.0474	2450.
8	O_3	$= O1D$	vary	
9	O_3	$= O$	$0.042 \times k_1$	
10	$O1D + M$	$= O + M$	42900.0	-100.
11	$O1D + H_2O$	$= OH + OH$	326000.0	
12	$O_3 + OH$	$= HO_2$	100.0	940.
13	$O_3 + HO_2$	$= OH$	3.0	580.
14	$NO_3 + NO$	$= NO_2 + NO_2$	28100.0	-250.
15	$NO_3 + NO_2$	$= NO + NO_2$	0.59	1230.
16	$NO_3 + NO_2 + M$	$= N_2O_5 + M$	1776.0	-226.
17	$N_2O_5 + H_2O$	$= HNO_3 + HNO_3$	1.9-6	
18	$N_2O_5 + M$	$= NO_3 + NO_2 + M$	3.12-6	10840.
19	$NO + NO_2 + H_2O$	$= HNO_2 + HNO_2$	1.6-11	
20	$HNO_2 + HNO_2$	$= NO + NO_2 + H_2O$	1.5-5	
21	HNO_2	$= NO + OH$	$0.18 \times k_1$	
22	$NO_2 + OH + M$	$= HNO_3 + M$	0.0163	-560.
23	$NO + OH + M$	$= HNO_2 + M$	0.00977	-427.
24	$HO_2 + NO$	$= OH + NO_2$	12300.0	-240.
25	$NO + NO + O_2$	$= NO_2 + NO_2$	7.28-10	-530.
26	H_2O_2	$= OH + OH$	$0.0014 \times k_1$	
27	$OH + H_2O_2$	$= HO_2$	2520.0	187.
28	$OH + HNO_2$	$= NO_2$	9770.0	
29	$OH + HNO_3$	$= NO_3$	192.0	-778.

TABLE 1 (continued)

	REACTIONS[a]		RATE CONSTANTS[b]	ACTIVATE ENERGY (K)[c]
30	NO_3	= NO_2 + O	26.0 x k_1	
31	NO_3	= NO	4.6 x k_1	
32	HO_2 + HO_2	= H_2O_2	4144.0	-1150.
33	HO_2 + HO_2 + H_2O	= H_2O_2 + H_2O	0.218	-5800.
34	HO_2 + NO_2 + M	= PNA + M	0.00163	-617.
35	PNA + M	= HO_2 + NO_2 + M	5.12-6	10420.
36	OH + CO + M	= HO_2 + M	4.0-4	
37	FORM + HO_2	= FROX	14.8	
38	FORM + OH	= HO_2 + CO	15000.0	
39	FORM	= HO_2 + HO_2 + CO	vary	
40	FORM	= CO	vary	
41	FORM + O	= OH + HO_2 + CO	237.0	1550.
42	FORM + NO_3	= HNO_3 + HO_2 + CO	0.93	
43	FROX + NO	= FACD + NO_2 + HO_2	10400.0	
44	FROX	= HO_2 + FORM	90.0	
45	ALD2 + O	= C_2O_3 + OH	636.0	986.
46	ALD2 + OH	= C_2O_3	24000.0	-250.
47	ALD2 + NO_3	= C_2O_3 + HNO_3	3.7	
48	ALD2	= MEO_2 + HO_2 + CO	vary	
49	ALD2 + HO_2	= MEO_2 + FORM	5.0	
50	C_2O_3 + NO	= MEO_2 + NO_2	16500.0	-250.
51	C_2O_3 + NO_2	= PAN	9000.0	-250.
52	PAN	= C_2O_3 + NO_2	0.0222	14000.
53	MEO_2 + NO_2 + M	= MPNA + M	0.006	-735.
54	MPNA + M	= MEO_2 + NO_2 + M	9.2-5	10400.
55	MEO_2 + NO	= MEO + NO_2	11000.0	-180.
56	MEO + NO	= MNIT	44400.0	-200.
57	MEO + NO	= FORM + HO_2 + NO	1920.0	
58	MEO + NO_2	= MEN3	22200.0	
59	MEO + O_2	= FORM + HO_2	1.88	1313.

TABLE 1 (continued)

	REACTIONS[a]		RATE CONSTANTS[b]	ACTIVATE ENERGY (K)[c]
60	MEN3 + OH	= FORM + NO_2	2220.0	360.
61	MNIT + OH	= FORM + NO	2370.0	340.
62	MNIT	= MEO + NO	0.3 x k_1	
63	MEO_2 + MEO_2	= MEO + MEO	175.0	-220.
64	MEO_2 + MEO_2	= FORM + MEOH	328.0	-220.
65	MEO_2 + C_2O_3	= MEO + MEO_2	4400.0	
66	C_2O_3 + C_2O_3	= MEO_2 + MEO_2	3700.0	
67	MEO_2 + HO_2	= PROX	8900.0	-1300.
68	C_2O_3 + HO_2	= PROX	9600.0	
69	AONE	= MEO_2 + C_2O_3	0.00004 x k_1	
70	AONE + OH	= ANO_2	580.0	
71	ANO_2 + NO	= NO_2 + FORM + C_2O_3	12000.0	
72	GLY	= CO + CO	0.0052 x k_1	
73	GLY	= CO + FORM	0.0016 x k_1	
74	GLY	= HO_2 + HO_2 + CO + CO	0.0007	
75	GLY + OH	= HO_2 + CO + CO	15000.0	
76	MGLY	= C_2O_3 + HO_2 + CO	0.02 x k_1	
77	MGLY + OH	= MGPX	26000.0	
78	MGPX + NO	= C_2O_3 + NO_2	12000.0	
79	OH + M	= MEO_2	2.1-5	
80	PAR + OH	= RO_2	150.0	
81	PAR + OH	= RO_2R	1000.0	
82	RO_2 + NO	= NO_2 + HO_2 + ALD2 + X	12000.0	
83	RO_2R + NO	= NO_2 + ROR	12000.0	
84	RO_2R + NO	= NTR	1000.0	
85	ROR + NO_2	= NTR	22000.0	
86	ROR	= KET + HO_2	150000.0	
87	ROR	= ALD2 + D + X	90000.0	7000.
88	ROR	= AONE + D + X + X	240000.0	
89	X + PAR		10000.0	

TABLE 1 (continued)

	REACTIONS[a]		RATE CONSTANTS[b]	ACTIVATE ENERGY (K)[c]
90	D + PAR	= RO_2	3000.0	
91	D + PAR	= AO_2 + X + X	7000.0	
92	D + KET	= C_2O_3 + X	10000.0	
93	AO_2 + NO	= NO_2 + HO_2 + AONE	12000.0	
94	KET	= C_2O_3 + RO_2 + X + X	0.0003 x k_1	
95	O + OLE	= MEO_2 + C_2O_3 + X	300.0	324.
96	O + OLE	= RO_2 + HO_2 + CO + X	880.0	324.
97	O + OLE	= ALD2	4740.0	324.
98	OH + OLE	= MEO_2 + ALD2 + X	42000.0	-537.
99	O_3 + OLE	= ALD2 + CRIG + X	0.0054	1897.
100	O_3 + OLE	= FORM + MCRG + X	0.0054	1897.
101	O_3 + OLE	= ALD2 + HOTA + X	0.0036	1897.
102	O_3 + OLE	= FORM + HTMA + X	0.0036	1897.
103	NO_3 + OLE	= PNO_2	11.4	
104	O + ETH	= MEO_2 + HO_2 + CO	1080.0	800.
105	OH + ETH	= MEO_2 + FORM	12000.0	-382.
106	O_3 + ETH	= FORM + CRIG	0.001	2840.
107	O_3 + ETH	= FORM + HOTA	0.0017	2840.
108	HOTA		25.0	
109	HOTA	= CO	58.0	
110	HOTA	= HO_2 + HO_2	10.0	
111	HOTA	= FACD	7.0	
112	HTMA		200.0	
113	HTMA	= MEO_2 + CO + OH	400.0	
114	HTMA	= MEO_2 + HO_2	320.0	
115	HTMA	= HO_2 + CO + FORM + HO_2	80.0	
116	CRIG + NO	= FORM + NO_2	10000.0	
117	CRIG + NO_2	= FORM + NO_3	1000.0	
118	CRIG + H_2O	= FACD	0.006	
119	CRIG + FORM	= OZD	30.0	

TABLE 1 (continued)

	REACTIONS[a]		RATE CONSTANTS[b]	ACTIVATE ENERGY (K)[c]
120	CRIG + ALD2	= OZD	30.0	
121	MCRG + NO	= ALD2 + NO_2	10000.0	
122	MCRG + NO_2	= ALD2 + NO_3	1000.0	
123	MCRG + H_2O	= ACAC	0.006	
124	MCRG + FORM	= OZD	30.0	
125	MCRG + ALD2	= OZD	30.0	
126	PNO_2 + NO	= DNIT	1000.0	
127	PNO_2 + NO	= NTR + HO_2 + NO_2	10000.0	
128	TOL + OH	= OPEN + GLY	5500.0	
129	TOL + OH	= PHEN + HO_2 + PAR	3500.0	
130	TOL + OH	= BO_2	750.0	
131	OPEN + NO	= NO_2 + HO_2 + MGLY + GLY	10000.0	
132	PHEN + NO_3	= PHO + HNO_3	14000.0	
133	BZA + OH	= BZO_2	20000.0	
134	BZO_2 + NO_2	= PBZN	2500.0	
135	BZO_2 +NO	= NO_2 + PHO_2 + CO	3700.0	
136	BO_2 + NO	= NO_2 + BZA + HO_2	12000.0	
137	PBZN	= BZO_2 + NO_2	0.022	14000.
138	BZA	= PROD	0.004 x k_1	
139	PHO + NO_2	= NPHN	20000.0	
140	PHO_2 + NO	= NO_2 + PHO	12000.0	
141	XYL + OH	= XYLO	2000.0	
142	XYLO + NO	= NO_2 + HO_2 + TLA	12000.0	
143	TLA + OH	= TLO_2	20000.0	
144	TLO_2 + NO	= NO_2 + PHO + PAR + PAR	4000.0	
145	XYL + OH	= HO_2 + PHEN + PAR + PAR	10000.0	
146	XYL+ OH	= OPEN + MGLY	24000.0	
147	ISOP + O	= OLE + ALD2	11160.0	
148	ISOP + O	= IS01 + CO + HO_2	11500.0	
149	ISOP + O	= IS02 + CO + HO_2	2750.0	

TABLE 1 (concluded).

	REACTIONS[a]		RATE CONSTANTS[b]	ACTIVATE ENERGY (K)[c]
150	ISOP + O	= KET + OLE + PAR	2700.0	
151	ISOP + OH	= IS03	84000.0	
152	ISOP + OH	= IS04	42000.0	
153	ISOP + O_3	= INT	0.018	
154	ISOP + NO_3	= ISNT	165.0	
155	IS01 + NO	= NO_2 + HO_2 + MACR	12000.0	
156	IS02 + NO	= NO_2 + HO_2 + MVK	12000.0	
157	IS03 + NO	= NO_2 + HO_2 + MVK + FORM	10000.0	
158	IS03 + NO	= ISN1	1500.0	
159	IS04 + NO	= NO_2 + HO_2 + MACR + FORM	10000.0	
160	IS04 + NO	= ISN2	1500.0	
161	ISNT + NO	= DNIT	10000.0	
162	INT	= MACR + FORM	9.0	
163	INT	= MVK + FORM + HO_2 + HO_2	4.0	
164	INT	= FORM + CO + OZD	1.2	
165	INT	= FORM + HO_2 + HO_2 + OZD	5.8	
166	MVK	= OLE + KET	1.0	
167	MVK	= ETH + KET	1.0	
168	MACR	= ALD2 + ETH + X	1.0	
169	IS03 + HO_2	= PROX	10000.0	
170	IS04 + HO_2	= PROX	10000.0	

[a] The species used are listed separately in Tables 3-8.

[b] All rate constants are in appropriate ppm and min units at 298K and one atmosphere of air. That is, all unimolecular and photolysis reactions (+ hν) are in units of min^{-1}; all bimolecular reactions are in units of ppm^{-1} min^{-1}; and all termolecular reactions are in units of ppm^{-2} min^{-1}. Rate constants designated as "vary" are defined in Table 2.

[c] The numbers listed are Arrhenious temperature coefficients in degrees Kelvin for B in the expression $k_T = k_{298} \exp(B \times (\frac{1}{298} - \frac{1}{T}))$.

TABLE 2. Photolysis reaction rates used in the ICRS relative to NO_2 photolysis.

Zenith Angle	$ALD2 + h\nu \rightarrow MEO2 + HO2 + CO$	$FORM + h\nu \rightarrow CO$	$FORM + h\nu \rightarrow HO2 + CO$	$O_3 + h\nu \rightarrow O^{1D}$
0	6.44E-4	2.71E-3	3.76E-3	4.66E-3
10	6.24E-4	2.70E-3	3.75E-3	4.55E-3
20	6.05E-4	2.61E-3	3.70F-3	4.16E-3
30	5.40E-4	2.48E-3	3.60E-3	3.53E-3
40	4.73E-4	2.28E-3	3.46E-3	2.77E-3
50	3.74E-4	2.01E-3	3.26E-3	1.92E-3
60	2.74E-4	1.64E-3	2.99E-3	1.11E-3
70	1.91E-4	1.25E-3	2.59E-3	4.76E-4
78	1.08E-4	9.15E-4	2.29E-3	2.10E-4
86	5.40E-5	6.90E-4	2.18E-3	1.12E-4

TABLE 3. Species in the ICRS Mechanism.

Symbol	Definition
NO_2	--
NO	--
NO_3	--
N_2O_5	--
HNO_2	--
HNO_3	--
PNA	HO_2NO_2
O1D	O(3P)
O1D	--
O_2	--
O_3	--
M	$O_2 + N_2$
MNIT	CH_3ONO
MEN3	CH_3ONO_2
MPNA	CH_3OONO_2
PAN	$CH_3CO_3NO_2$
OH	--
HO_2	--
H2O2	--
H_2O	--
CH_4	(lumped in rate constant of Rx 79)
FORM	HCHO
MEO2	CH_3O_2
MEO	CH_3O
MEOH	CH_3OH (appears only as a product)
CO	--
FROX	HO_2CH_2O
ALD2	CH_3CHO
C2O3	CH_3CO_3
PROX	CH_3CO_3H
FACD	Formic acid
AONE	Acetone
ANO_2	$CH_3C(O)CH_2O_2$
GLY	Glyoxal
MGLY	Methylglyoxal
MGPX	$CH_3(CO)CO_3$

TABLE 4. Species contained in the ethene mechanism.

Symbol	Definition
ETH	Ethene
CRIG	Crigee intermediate
HOTA	Energy-rich "hot" formic acid
FACD	Formic acid
OZD	Ozonide

TABLE 5. Species contained in toluene and m-xylene mechanism.

Symbol	Definition
TOL	Toluene
OPEN	Ring-opening precursor radical
PHEN	Phenyl-type product (cresol for toluene)
BO2	OH abstraction peroxy precursor to benzaldehyde
PHO	Phenoxy radical
BZA	Benzaldehyde
BZO2	Peroxy benzoyl radical
PBZN	Peroxy benzoyl nitrate
PHO2	Peroxy phenyl radical
NPHN	Nitrophenol
XYL	Xylene
XYLO	OH abstraction peroxy precursor to tolualdehyde
TLA	Tolualdehyde
TLO2	Methyl-peroxybenzoyl radical

TABLE 6. Species involved in the oxidation of paraffin.

Symbol	Definition
PAR	1-Carbon paraffin group
RO_2	Primary alkyl peroxy radical with C<4
RO_2R	See text--alkyl peroxy and long-chain radicals
ROR	Alkoxyl radicals
KET	Ketones other than acetone
AONE	Acetone
D	Fictitious species to account for alkoxyl radical decomposition and isomerization
A02	Peroxy isopropyl radical
X	Fictitious steady-state species to maintain carbon balance
NTR	Organic nitrate
A02	Isopropyl peroxy radical

TABLE 7. Species involved in the oxidation of olefin.

Symbol	Definition
OLE	2-carbon double-bond group
CRIG	Crigee intermediate (dioxirane)
MCRG	Methyl Crigee
PNO_2	Peroxy isoproyl nitrate radical
HOTA	Energy-rich formic acid
HTMA	Energy-rich acetic acid
DNIT	Organic dinitrate
NTR	Organic nitrate
FACD	Formic acid
OZD	Ozonide
ACAC	Acetic acid

TABLE 8. Species contained in the isoprene mechanism.

Symbol	Definition
ISOP	Isoprene
IS01	O atom peroxy adduct to terminal bond
IS02	O atom peroxy adduct to internal bond
IS03	OH peroxy adduct to internal bond
IS04	OH peroxy adduct to terminal bond
INT	A molozonide
ISNT	Nitrated peroxy intermediate
MACR	Methylacrolein
MVK	Methyl vinyl ketone
ISN1	Nitrate product
ISN2	Nitrate product

The use of a carbon-bond mechanism offers several advantages over mechanisms that use a hydrocarbon molecule to represent an entire class of organic compounds. It allows the conservation of carbon mass and also leads to a more accurate representation of kinetic data for an entire class of organic compounds. For example, the rates of the reactions of olefin molecules with OH radicals cover a wide range of values depending on the olefin, but many olefins have similar rates per attack on the olefin bond. The use of a carbon-bond representation allows one to simulate this spread of reactivity more accurately than does a lumped molecular representation which might approximate all olefin-OH reaction molecular rates with a single value. A disadvantage of the carbon-bond representation is that intramolecular processes such as decomposition and side-chain activation may require adept treatment and extra documentation (Whitten, 1983).

THE HIERARCHICAL CONCEPT

The hierarchical approach to mechanism development was first outlined for a series of mechanisms in Whitten et al. (1979); a more recent description is contained in Whitten (1983). The most important objective of this approach is to minimize compensating errors in the final overall smog mechanism. Also, the approach allows each of the organic components of the mechanism to be developed and validated independently.

A reaction set such as the ICRS, which includes both carbonyl and inorganic smog reactions, is in itself a complete reaction scheme that can be independently tested against smog chamber data. As discussed by Whitten (1983), such a reaction scheme contains all the essential components required to generate photochemical ozone in the lower troposphere. These essential components include nitrogen oxides, a hydrogen-containing radical source, and a means of converting OH radicals to HO_2, which, in turn, converts NO to NO_2 and OH, thus completing a chain process. Hence, smog chamber experiments containing only a nitrogen oxide and one or more of the five carbonyls included in the ICRS (formaldehyde, acetaldehyde, acetone, glyoxal, and methylglyoxal) will generate photochemical ozone at rates sufficiently above background levels to test this ICRS or any other inorganic-plus-carbonyl scheme.

The use of smog chamber data to test only an overall mechanism such as the CBM-XR of this particular study does not address the question of compensating errors. For example, an incorrect treatment of aromatics chemistry might be compensated for by incorrect treatment of the dicarbonyl products formed from aromatics (Tuazon et al., 1984). However, independent smog chamber experiments containing a dicarbonyl as the only organic have been performed and successfully simulated using the ICRS of

Table 1. Thus, the overall performance of the dicarbonyl subset must be close to "reality." Of course, errors can still exist in the yield of these highly reactive dicarbonyls from aromatics. However, we now know that any other products that might be formed appear to have a reactivity similar to that of the dicarbonyls. Therefore, any excess dicarbonyls can, for the time being, serve as surrogates for other compounds that might form from the aromatics chemistry.

The hierarchical approach is also helpful in explicit mechanism development for specific organic species. For example, in the development of an explicit scheme for isoprene, the chemistry of intermediate compounds such as methacrolein (MACR) and methyl vinyl ketone (MVK) was identified (Killus and Whitten, 1984a). As a result, smog chamber experiments were requested which used methyl vinyl ketone or methacrolein as the only organic. These experiments were subsequently performed in the University of North Carolina (UNC) smog chamber and simulated using the ICRS and reactions specific to these organics (Killus and Whitten, 1984b). Hence, intermediate levels in the hierarchy are associated with the chemistry of intermediate organic products, and these subsets of the overall chemistry can be independently tested.

SPECIFIC FEATURES OF THE CBM-XR

In keeping with the hierarchical approach just outlined, the overall CBM-XR mechanism assembled in Table 1 is organized into the following subsets:

Inorganic Chemistry

Reactions 1 through 36 describe the atmospheric chemistry of species that contain only oxygen, nitrogen, and hydrogen atoms and one reaction involving CO.

Common Carbonyl Chemistry

Reactions 37 through 78 describe the detailed chemistry for the common carbonyl compounds formaldehyde, acetaldehyde, acetone, glyoxal, and methylglyoxal. Reaction 79 describes the chemistry of methane. Since methane in the atmosphere does not decay from a constant level of 1.6 ppm, the concentration of methane has been lumped into the rate constant. These first 79 reactions provide enough overall chemistry to generate photochemical ozone and PAN, and can therefore be independently tested against smog chamber experiments.

Paraffinic or Single-Bonded Carbon Chemistry

Reactions 80 through 94 describe a typical mixture of paraffins, from butane to decane. The single-bonded constituents of other types of molecules, such as olefins and aromatics, are also treated as the one-carbon PAR species.

Olefin Chemistry

Reactions 95 through 127 constitute the subset of reactions specific to molecules containing double bonds. Since such molecules can have a wide range of reactivity, the atmospheric mix of olefins in the CBM-XR is treated in three different ways. First, ethene, which is the least reactive of the olefins, is treated explicitly. The ethene mechanism has no significant condensation except for the elimination of the pathway to glycolaldehyde and its subsequent chemistry. The glycolaldehyde yield from the OH attack on ethene appears to be about 22 percent (Niki et al., 1981). Elimination of this pathway is equivalent to assuming the alternative products to be equal in reactivity to glycolaldehyde. The accuracy of this assumption is not clear at this time since smog chamber data for glycolaldehyde are not yet available.

Second, terminal olefins such as propene are of intermediate reactivity and are handled in condensed form via the species OLE. OLE is a two-carbon lumped structure species that represents the carbon bond found in 1-olefins. Finally, highly reactive olefins such as those with internal double bonds (e.g., cis-2-butene) are treated by assuming that they have already reacted in the atmosphere to form two higher aldehydes (i.e., 2 ALD2). This condensation has been successfully demonstrated in Whitten et al. (1979) and was recommended for use with the first version of the Carbon-Bond Mechanism (Whitten et al., 1980).

Aromatics Chemistry

Reactions 128 through 146 provide a moderately condensed treatment of aromatic hydrocarbons. Two levels of reactivity based on toluene chemistry (Killus and Whitten, 1982) and m-xylene chemistry (Killus and Whitten, 1983) are used. The toluene chemistry is used to represent the mono-substituted benzenes (toluene, ethylbenzene, propyl-benzenes, etc.), whereas the m-xylene chemistry is used to represent the highly reactive multiple-substituted benzenes (xylenes, ethyltoluenes, trimethylbenzenes, etc.).

Isoprene Chemistry

A semicondensed version of the explicit scheme for isoprene reported by Killus and Whitten (1984b) has been developed and is shown in reactions 147 through 170 of Table 1. The first three reactions describe the chemistry of O atom attack on isoprene. The ISO1 and ISO2 intermediates formed in Reactions 148 and 149 are assumed to react with NO to yield methylacrolein (MACR) and methyl vinyl ketone (MVK) as shown in Reactions 155 and 156. Isoprene also reacts with OH (Reactions 151 and 152) to form the peroxy-OH adducts ISO3 and ISO4. These species chiefly react with NO to form NO_2, HO_2, FORM, and MVK or MACR (Reactions 157 and 159). A fraction of the ISO3 and ISO4 intermediates, however, are assumed to react with NO to form stable nitrates (Reactions 158 and 160). Both MACR and MVK can undergo a variety of reactions that involve a number of intermediates. An accurate treatment of their chemistry would introduce more species into the mechanism than could be tolerated in a regional oxidant model. It was found, however, that good agreement to an explicit isoprene mechanism developed by Killus and Whitten (1984b) could be achieved by assuming that MACR and MVK decompose to a variety of aldehyde, ketone, and olefin products. The product distribution and the rate constants for this decomposition that gave the closest fit to the explicit isoprene mechanism are shown in Reactions 166-168. The important reaction of isoprene with NO_3 (Reaction 154) is also included in the CBM-XR. The nitrated peroxy intermediate (ISNT) formed in this reaction is assumed to react with NO to form a stable dinitrate (Reaction 161).

It would have been possible to develop a fully condensed version of isoprene, utilizing the olefinic character of this species so that no new species would be required. That is, one molecule of isoprene could have been treated as one each of the carbon-bond species OLE, FORM, and ALD2, in a process similar to the scheme recommended by Killus and Whitten (1984b). For the Regional Oxidant Model, however, we treated isoprene explicitly as a separate species because (1) we wished to know specifically what the isoprene concentration was since isoprene is a biogenic compound and must not be confused with anthropogenic species, and (2) we wished to treat nighttime reactions of isoprene with O_3 and NO_3, which a surrogate mixture would not be able to reproduce. Also, the special level of condensation chosen should be more accurate than a fully condensed version.

SUMMARY

The mechanism shown in Table 1 is designed to model the entire atmospheric mix of organics. Also, because the mechanism is grouped into components, it is fairly adaptable to substitution, updates, and additions. An example is the condensed version of the chemistry of the natural hydrocarbon, isoprene (Killus and Whitten, 1984), which has been added to the CBM-X yielding the CBM-XR mechanism reported here. Similarly, a newer version of aromatics chemistry might be substituted for the aromatics subset. However, any updates and substitutions should be accompanied by a revalidation procedure to ensure the fidelity of the precautions originally taken in the development of the CBM-XR to minimize compensating errors between the various subsets and between each subset and the basic ICRS set.

SECTION 3

VALIDATION OF THE CBM-XR

INTRODUCTION

The hierarchical method of mechanism validation was applied to CBM-XR through a series of simulations of selected smog chamber experiments. The validation of the first 146 reactions, which constitute the urban mechanism known as the CBM-X, are described in Whitten, Killus, and Johnson (1985). Only two extra validation steps were required to test the CBM-XR: (1) the mechanism had to be validated for its isoprene chemistry and (2) the mechanism had to be tested for its ability to simulate multiday and nighttime chemistry. These two additional steps were needed so that the mechanism could be used in the ROM to model multiday episodes on a regional scale.

In Whitten, Killus, and Johnson (1985), the components of the CBM-X were independently validated against smog chamber data. The overall mechanism was then tested against a new data set using auto exhaust data. The inorganic and carbonyl reaction set (ICRS), which includes the chemistry of formaldehyde, acetaldehyde, PAN, and methyl glyoxal, was validated with numerous experiments involving those compounds. The explicit mechanisms used in the CBM-X for ethene, toluene, and m-xylene were also independently validated against smog chamber data. The carbon-bond formulation used for 1-olefins was compared to an explicit, validated mechanism for propene, and thus can also be considered to be a validated subcomponent of the full mechanism. The carbon-bond formulation for single-bonded species or alkyl groups (PAR) was compared to explicit, validated mechanisms for n-butane and 2,3-dimethylbutane.

The overall CBM-X mechanism has successfully simulated a new series of auto exhaust experiments that use a variety of conditions. These experiments were performed in the outdoor dual chamber facility of the University of North Carolina, which is a well-characterized chamber having extensive analytical capabilities. The conditions used for these experiments included a variety of automobiles, fuels, driving cycles, and methods of sample preparation.

ISOPRENE VALIDATION

The isoprene chemistry was developed from the detailed and validated mechanism of Killus and Whitten (1984b). The condensed set of reactions used in the CBM-XR was then tested against the same set of smog chamber experiments used to validate the explicit isoprene mechanism. Ten isoprene/NO_x smog chamber runs were modeled to test Reactions 147-170 of the CBM-XR. In addition, two experiments that used methyl vinyl ketone and NO_x as the initial reactants and two using methacrolein/NO_x were also simulated. The initial conditions for these runs and the simulation profiles are presented in Appendix B. Table B-1 contains a comparison of the predicted and observed O_3 obtained with both the explicit mechanism and the generalized CBM-XR. In general, the simulations using the condensed scheme agree well with the experimental data.

In some cases there were differences in quality between the predictions obtained using the fully explicit chemistry and those obtained using the partially condensed scheme. These differences can be attributed to the reactions of the isoprene-related chemistry because both versions use the same inorganic and carbonyl reaction set (ICRS). The term "quality" is used here because the primary ozone peaks are often simulated quite accurately and similarly by both versions of the isoprene chemistry. However, the data show secondary ozone peaks and unusual ozone oscillations that are not easily quantified. The simulations using the fully explicit scheme of Killus and Whitten (1984b) are better able to explain the secondary peaks and unusual ozone oscillations found in the observed data than are the simulations presented in Appendix B.

MULTIDAY VALIDATION

The study of regional oxidant formation requires a kinetics mechanism that can accurately simulate multiday smog events in a computer model. Therefore, the kinetics mechanism must include both reactions that may be important during nighttime and that are involved in the long organic photooxidation process in which several levels of intermediate compounds are formed. Although the ultimate products of organic photooxidation are usually CO and H_2O, there may be some stages of the process in which the reactivity of intermediate products does not significantly affect the overall observable chemistry of the atmospheric mixture of organics.

A new set of smog chamber data obtained by the University of California at Riverside (UCR) was simulated during this project. These experiments utilizied a special surrogate mixture of hydrocarbons designed to approximate the main species in urban atmospheres. The composition of this eight hydrocarbon mixture, as reported by Carter et al. (1985), is given in Table 9. A detailed description of the facility and run conditions is also given in Carter et al. (1985). Briefly, the smog chamber used at UCR is an outdoor dual-sided Teflon chamber, approximately 50,000 liters in size. The set of outdoor experiments performed in 1983 consisted of multiday runs using various hydrocarbon to NO_x ratios. In some runs NO_x was added on second or subsequent days to resume the production of ozone.

The initial conditions used to simulate the 1983 outdoor data are presented in Table C-1 of Appendix C in approximately chronological order. Since isobutene was an important compound in the urban mixture, its chemistry was treated separately. Hence, the reactions shown in Table 10 were added to the CBM-XR mechanism to simulate the UCR data.

All 22 experiments listed in Table C-1 were modeled in this study. Some of these experiments were carried out for as long as four days. In some cases, additional NO was injected on the subsequent days. Simulations for most of these experiments are presented in Appendix C. A number of the runs conducted in the UCR study were replicates of earlier runs. In an effort to reduce the size of this report, occasionally the results obtained for only one of these replicate runs are included in the Appendix.

As is evident from the simulations presented in Appendix C, the CBM-XR mechanism simulates the experiments quite closely overall. However, the chronological sequence indicates that the early runs are overpredicted, while the last few runs are slightly underpredicted. Since some of the early and late runs used similar initial conditions there appears to be a problem with conditioning of the Teflon bag. On the other hand, there may be a seasonal effect not properly simulated by the CBM-XR. In any case, such an effect has not been noticed in simulations of a series of experiments performed at the UNC chamber. The UNC auto exhaust experiments were used to validate the first 146 reactions of the CBM-XR as reported by Whitten, Killus, and Johnson (1985). The Teflon chamber at UNC has been in service for 10 years, whereas the UCR chamber used in 1983 runs was new.

There was some concern about the quality of the nighttime chemistry currently in the CBM-XR. However, the use of a somewhat high value for the rate constant of Reaction 17 ($N_2O_5 + H_2O$) of 1.5×10^{-5} ppm^{-1} min^{-1} provided good results. On the one hand, this rate constant may be appropriate for this chamber since this reaction is known to be affected by surfaces. On the other hand, the high value used may be masking or simulating other reactions that are missing from the CBM-XR. Further studies

TABLE 9. Composition[a] of the "Urban Surrogate" Hydrocarbon Mixture.

Hydrocarbon	Percent Carbon	$\frac{\text{ppm Component}}{\text{ppmC Surrogate}}$
Ethene	5.0	0.025
Propene	5.6	0.019
Isobutene	14.3	0.036
n-Butane	15.8	0.040
n-Pentane	19.6	0.039
Isooctane	14.8	0.018
Toluene	12.6	0.018
m-Xylene	12.3	0.015

[a] Based on analyses of cylinder gases employed in outdoor chamber experiments carried out in 1983.

TABLE 10. Isobutene Mechanism

IBTN + OH	= MEO_2 + AONE	75000.
IBTN + O	=	20000.
	= $2HO_2$ + CO + AONE	5000.
IBTN + O_3	= AONE + HOTA	.005
	= AONE + CRIG	.009
	= 2FORM + HO_2 + C_2O_3	.006
IBTN + NO_3	= PNO_2 + FORM	250.

are needed to determine the "proper" value to be used in atmospheric models.

A comparison of the predicted and observed O_3 for each of the 22 runs modeled in this study is presented in Table 11. The data in Table 11 reflect either the apparent startup problems with the chamber or seasonal/temperature problems with the mechanism. Taking into account all 48 side/days, the overal bias is +0.05 ppm ozone; however, when only the 34 non-July side/days are used, the bias is only + 0.01 ppm ozone and the standard deviation is 0.04 ppm. The bias for the 14 July side/days only is +0.12 ppm ozone and the standard deviation is 0.13 ppm ozone. Simulation of the time to ozone maximum is better than 5 minutes, on the average. Simulation of the time to ozone maximum is less critical in outdoor experiments because changes in solar radiation play a major role in defining maxima, whereas indoor chambers, which have a constant light flux, show a high sensitivity to organic reactivity in defining ozone maxima.

The most anomalous of the data shown in Appendix C appear to be the data for acetaldehyde, which indicates that considerable concentrations are generated on multiple-day experiments. Also, the NO_x data cannot be explained as NO_2 since ozone would be expected to decay at night if NO_2 is present, and ozone should increase during daylight if both NO_2 and organic are present. In many instances, the observed "NO_2" may in fact be other compounds such as N_2O_5, PAN, NO_3, and HNO_3. Future studies should include more extensive NO_x measurements to determine the actual species measured by the NO_2 instrument used for these experiments. The discrepancies in NO_x seen in this study suggest that many atmospheric NO_x experiments may not accurately measure NO_2.

TABLE 11. Comparison of experimental and observed ozone for the UCR multiday runs.

Run Number	Initial $[NO_x]$ (ppm)	Initial NO_2/NO_x Ratio	Initial HC/NO_x ppmC/ppm	Maximum O_3 (ppm)		Difference in O_3 Maximum	Time to Maximum O_3 (min)		Difference in time to Maximum
				Sim.	Meas.		Sim.	Meas.	
70783R	0.452	0.250	8.74	0.80	0.59	0.21	360	340	20
*70883R	-	-	-	0.59	0.35	0.24	0	0	0
72783R	0.380	0.316	20.09	0.90	0.73	0.17	220	210	10
*72883R	-	-	-	0.68	0.55	0.13	0	0	0
72783B	0.360	0.250	10.87	0.72	0.62	0.52	0.10	330	0
*72883B	-	-	-	0.52	0.47	0.05	0	0	0
80283R	0.410	0.390	4.55	0.24	0.17	0.07	300	300	0
*80383R	-	-	-	0.40	0.40	0.00	900	890	10
80283B	0.413	0.395	9.78	0.79	0.68	0.11	300	300	0
*80383B	-	-	-	0.53	0.48	0.05	0	0	0
82483R	0.365	0.384	9.44	0.65	0.65	0.00	315	315	0
*82583R	-	-	-	0.50	0.48	0.02	920	900	20
*82683R	-	-	-	0.41	0.35	0.06	0	0	0
82483B	0.760	0.289	4.65	0.16	0.16	0.00	315	315	0
83083R	0.740	0.351	7.03	0.71	0.71	0.00	315	315	0
*83183R	-	-	-	0.51	0.53	-0.02	900	865	35
*90183R	-	-	-	0.41	0.44	-0.03	0	0	0
83083B	0.390	0.692	8.98	0.65	0.68	-0.03	310	330	-20
*83183B	-	-	-	0.47	0.52	-0.05	0	0	0
*90183B	-	-	-	0.38	0.36	0.02	0	0	0
90783R	0.360	0.250	9.73	0.65	0.59	0.06	370	350	20
90783B	0.360	0.250	9.76	0.65	0.61	0.04	370	350	20
*90883B	-	-	-	70.60	0.60	-	960	960	0
92183R	0.715	0.105	9.13	0.65	0.73	-0.08	280	275	5
*92283R	-	-	-	0.37	0.40	-0.03	0	0	0
*92383R	-	-	-	0.30	0.29	0.01	0	0	0
92183B	0.395	0.165	8.83	0.49	0.53	-0.04	275	280	-5
*92283B	-	-	-	0.31	0.35	-0.04	0	0	0
*92383B	-	-	-	0.26	0.26	0.00	0	0	0
92883R	0.390	0.205	8.91	0.24	0.24	0.00	320	300	20
92883B	0.180	0.167	19.46	0.40	0.39	0.01	320	320	0
100483R	0.373	0.201	9.32	0.31	0.31	0.00	305	325	-20
*100583R	-	-	-	0.25	0.21	0.04	930	900	30
100483B	0.170	0.235	20.64	0.39	0.38	0.01	295	295	0
*100583B	-	-	-	0.30	0.32	-0.02	0	0	0
*100683B	-	-	-	0.45	0.38	0.07	900	900	0
101083B	0.140	0.300	24.91	0.39	0.39	0.00	250	250	0
*101183B	-	-	-	0.61	0.52	0.09	920	920	0
*101283B	-	-	-	0.52	0.46	0.06	780	800	-20
*101383B	-	-	-	0.41	0.37	0.04	0	0	0
71283R	0.415	0.205	8.77	0.84	0.71	0.13	360	340	20
*71383R	-	-	-	0.59	0.55	0.04	0	0	0
71283B	0.415	0.205	8.77	0.84	0.67	0.17	360	345	15
*71383B	-	-	-	0.58	0.50	0.08	0	0	0
71983R	0.475	0.369	8.64	0.84	0.74	0.10	345	340	5
*72083R	-	-	-	0.60	0.55	0.05	0	0	0
71983B	0.500	0.390	8.13	0.88	0.78	0.10	350	350	0
72083B	-	-	-	0.72	0.63	0.09	900	900	0

* Continuation from previous day

SECTION 4

CONDENSATION OF THE CBM-XR

The CBM-XR mechanism shown in Table 1 is appropriate for describing oxidant formation on a regional scale. However, the mechanism can only be used in atmospheric models that do not require a severely condensed reaction scheme. The EPA Regional Oxidant Model (ROM) requires a more condensed mechanism than the CBM-XR. Therefore, it was necessary to develop a condensed version of the CBM-XR for use in the ROM. A five-step approach was followed to achieve the condensation of this mechanism, which is called the CBM-RR for reduced regional mechanism. Each of these steps is described in detail in the following paragraphs.

STEP (1): LUMPING

The first step in the condensation process was to eliminate the species M (air) and O_2. The concentration of these reactants is constant so that their concentration can be absorbed into the rate constants:

$$M = 10^6 \text{ ppm}$$
$$O_2 = 2.1 \times 10^5 \text{ ppm}$$

For example, Reaction (2):

$$O + O_2 + M \rightarrow O_3 + M \qquad k = 2.22 \times 10^{-5} \text{ ppm}^{-2} \text{ min}^{-1}$$

can be rewritten as

$$O \rightarrow O_3 \qquad k = 4.65 \times 10^6 \text{ min}^{-1}$$

STEP (2): CREATION OF A UNIVERSAL PEROXY RADICAL

There are 13 different generalized peroxy radicals in the CBM-XR: ANO2, MGPX, RO2, AO2, OPEN, BO2, PHO2, XYLO, TLO2, ISO1, ISO2, RO2R, and PNO2.

The only fate of these radicals is reaction with NO to form NO_2 and a variety of products. It should be possible, therefore, to replace all 13 of these species with one universal peroxy radical--such as XO_2--that would oxidize NO to NO_2:

$$XO_2 + NO \rightarrow NO_2$$

The reactions in the CBM-XR that produce the 13 generalized radicals were then modified to include products other than NO_2 that are formed during oxidation. For example, consider Reactions 70 and 71 in the CBM-XR:

$$AONE + OH \rightarrow ANO_2 \tag{70}$$

$$ANO_2 + NO \rightarrow NO_2 + FORM + C_2O_3 \tag{71}$$

The radical ANO_2 can be replaced by XO_2 if the products of Reaction 70 are modified to include FORM and C_2O_3:

$$AONE + OH \rightarrow XO_2 + FORM + C_2O_3$$

$$XO_2 + NO \rightarrow NO_2$$

The only time such a substitute would produce a change in the predictions of the mechanism would be when the concentration of NO was near zero. In this case, FORM and C_2O_3 would still be produced in the mechanism even though no NO were available. However, ozone cannot be formed in the absence of NO; therefore, accumulation of FORM and C_2O_3 should not affect the ozone predictions of the CBM-RR. Tests of this condensation step are described at the end of this section.

Following the approach just outlined, the OH oxidation of methyl glyoxal, which is now represented as

$$MGLY + OH \rightarrow MGPX \tag{77}$$

$$MGPX + NO \rightarrow C_2O_3 + NO_2 \tag{78}$$

could be changed to

$$MGLY + OH \rightarrow XO_2 + C_2O_3$$

$$XO_2 + NO \rightarrow NO_2$$

In these examples, the two species ANO_2 and MGPX have been replaced by the single species XO_2. If the same approach is followed for the other generalized peroxy radicals, all 13 can be replaced with the single species XO_2, for a total reduction of 12 species from the species contained in the CBM-XR.

STEP (3): ELIMINATION OF STABLE PRODUCTS

A number of products formed in the CBM-XR are assumed to be stable. That is, no reactions are included for these species. Therefore they can be eliminated without altering the predictions of the mechanism. These stable products are NTR, FACD, OZD, PROX, MEOH, ACAC, DNIT, PROD, NPHN, and PROX. This condensation step eliminates 10 species from the mechanism.

STEP (4): ADDITIONAL SPECIES ELIMINATION

The sole fate of some species in the CBM-XR is unimolecular decay; that is, they do not undergo reaction with any other species. MACR is an example of a species whose sole fate is represented by Reaction 168:

$$\mathrm{MACR} \rightarrow \mathrm{ALD2} + \mathrm{ETH} + \mathrm{X} \tag{168}$$

MACR is formed in several reactions, including Reaction 162:

$$\mathrm{INT} \rightarrow \mathrm{MACR} + \mathrm{FORM} \tag{162}$$

MACR can be eliminated from Reaction 162 by replacing it with the products of Reaction 168:

$$\mathrm{INT} \rightarrow \mathrm{ALD2} + \mathrm{ETH} + \mathrm{X} + \mathrm{FORM}$$

Similarly, because the only fate of INT is unimolecular decay, this species can also be eliminated from the CBM-XR. The following species can be eliminated in this fashion: HOTA, HTMA, INT, MVR, and MACR.

Another species, X, can be eliminated by introducing the concept of a negative stoichiometric coefficient, i.e., a "negative product." Species X appears as a product of several reactions, including Reaction 82:

$$\mathrm{RO_2} + \mathrm{NO} \rightarrow \mathrm{NO_2} + \mathrm{HO_2} + \mathrm{ALD2} + \mathrm{X} \tag{82}$$

The sole function of species X is to maintain carbon balance by removing a carbon atom from the system. Its "chemistry" is represented by Reaction 89:

$$X + PAR \rightarrow \qquad (89)$$

Species X can be removed from Reaction 82 by introducing the negative product PAR:

$$RO_2 + NO \rightarrow NO_2 + HO_2 + ALD2 - PAR$$

One additional species can be eliminated from the mechanism by combining two species. Isoprene reacts with OH to generate two peroxy-OH adducts represented by ISO3 and ISO4:

$$ISOP + OH \rightarrow ISO3 \qquad k = 8.4 \times 10^4 \ ppm^{-1} \ min^{-1}$$

$$ISOP + OH \rightarrow ISO4 \qquad k = 4.2 \times 10^4 \ ppm^{-1} \ min^{-1}$$

Therefore, these reactions can be combined:

$$ISOP + OH \rightarrow 0.66 \ ISO3 + 0.33 \ ISO4 \qquad k = 1.26 \times 10^5 \ ppm^{-1} \ min^{-1}$$

We could then introduce the species ISO5 as equivalent to 0.66 ISO3 + 0.33 ISO4. In this fashion, ISO3 and ISO4 would be replaced by the single species ISO5. Thus, Step (4) eliminates seven additional species from the mechanism.

STEP (5): COMBINING REACTIONS

A number of species in the CBM-XR react by more than one pathway. For example, the photolysis of NO_3 is represented by:

$$NO_3 \rightarrow NO_2 + O \qquad k = 26.0 \times k_1 \ min^{-1}$$

$$NO_3 \rightarrow NO \qquad k = 4.6 \times k_1 \ min^{-1}$$

These two reactions can be combined into one:

$$NO_3 \rightarrow 0.85 \ NO_2 + 0.85 \ O + 0.15 \ NO \qquad k = 30.6 \times k_1 \ min^{-1}$$

Similarly, the two reactions of PAR with OH,

$$PAR + OH \rightarrow RO2 \qquad k = 150 \ ppm^{-1} \ min^{-1}$$

$$PAR + OH \rightarrow RO2R \qquad k = 1000 \ ppm^{-1} \ min^{-1}$$

can be replaced with a single reaction:

$$\mathrm{PAR + OH \rightarrow 0.13\ RO2 + 0.87\ RO2R} \qquad k = 1150\ \mathrm{ppm^{-1}\ min^{-1}}$$

Steps 1 through 5 result in the elimination of 31 species and 55 reactions. When all of these changes are made to the CBM-XR mechanism, the condensed mechanism CBM-RR shown in Table 12 is obtained. The CBM-XR has been reduced from 170 reactions with 78 species to 115 reactions containing 47 species.

It should be pointed out that this condensation of the CBM-XR does not affect the numerical output of the mechanism to any significant degree. Although 31 species have been eliminated in the CBM-RR, the original chemistry of the CBM-XR remains intact. The only modifications to the mechanism were the elimination of constant species, species that only appear as products, intentional steady-state species, and peroxy radicals, which react only with NO in the CBM-XR. Any possible difference between simulations using the full CBM-XR or the reduced-species version, CBM-RR, would be due either to the timing advance in secondary products that accompanies the peroxy radical reactions with NO, or numerical discrepancies stemming from the intentional steady-state species integration. The former type of discrepancy can only occur at near-zero NO concentrations when oxidant cannot form anyway. The latter type, if an error occurs, would indicate that the CBM-XR requires changes to further ensure that the intentional steady-state species are indeed in steady state. In this case, the CBM-RR would be the more accurate version.

To ensure that the condensed mechanism (CBM-RR) does indeed simulate atmospheric chemistry as well as the full CBM-XR, a computer simulation was performed with the CBM-RR. As discussed, the only conceivable change in simulation performance is associated with the use of the generalized peroxy radical XO_2. When NO is reduced to near zero, the condensation technique involving XO_2 advances the appearance of secondary products, which would appear in the CBM-XR only when NO is reintroduced into the simulation.

The UCR outdoor chamber experiment of 10-13 October 1983 was used to test the significance of this timing discrepancy between simulations using the CBM-RR and the CBM-XR. This four-day experiment ran out of NO each day, but fresh NO was introduced the last three days. The simulation results using the CBM-XR mechanism (Figures C-37 to C-40 in Appendix C) can be compared with the simulation results using the CBM-RR (Figures 1a through 1d in this section). The only discernible difference between the two sets of simulations seems to be slightly less reactivity at the end of the fourth day. The CBM-RR simulation produces identical ozone but slightly less PAN. Xylene (XYL) decay in the reduced mechanism is also slightly less.

TABLE 12. Condensed regional carbon-bond mechanism (CBM-RR).

	REACTIONS		RATE CONSTANT	ACTIVATION ENERGY (K)
1	NO2	= NO +O	vary	
2	O	= O3	4.65 X 10^{+6}	-690.
3	O3 +NO	= NO2	26.6	1430.
4	O +NO2	= NO	13800.	
5	O +NO2	= NO3	2320.	-600.
6	O +NO	= NO2	3120.	-411.
7	NO2 +O3	= NO3	0.0474	2450.
8	O3	= O1D	vary	
9	O3	= O	0.042	
10	O1D	= O	4.29 X 10^{+10}	-100.
11	O1D +H2O	= 2. OH	326000.	
12	O3 +OH	= HO2	100.	940.
13	O3 +HO2	= OH	3.0	580.
14	NO3 +NO	= 2. NO2	28100.	-250.
15	NO3 +NO2	= NO +NO2	0.59	1230.
16	NO3 +NO2	= N2O5	1780.	60.
17	N2O5+H2O	= 2. HNO3	1.9 X 10^{-6}	
18	N2O5	= NO3 +NO2	3.12	10840.
19	NO +NO2 +H2O	= 2. HNO2	1.6 X 10^{-11}	
20	HNO2+HNO2	= NO +NO2 +H2O	1.5 X 10^{-5}	
21	HNO2	= NO +OH	0.18 X k1	
22	NO2 +OH	= HNO3	16300.	-560.
23	NO +OH	= HNO2	9770.	-427.
24	HO2 +NO	= OH +NO2	12300.	-240.
25	NO +NO	= 2. NO2	1.52 X 10^{-4}	-530.
26	H2O2	= 2. OH	0.0014 X k1	
27	OH +H2O2	= HO2	2520.	187.
28	OH +HNO2	= NO2	9770.	
29	OH +HNO3	= NO3	192.	-778.
30	NO3	= .85NO2 +.85 O +.15NO	30.6 X k1	
31	HO2 +HO2	= H2O2	4144.	-1150.
32	HO2 +HO2 +H2O	= H2O2 +H2O	0.218	-5800.
33	HO2 +NO2	= PNA	1630.	-617.
34	PNA	= HO2 +NO2	5.12	10420.
35	OH +CO	= HO2	400.	
36	FORM+HO2	= FROX	14.8	
37	FORM+OH	= HO2 +CO	15000.	
38	FORM	= 2. HO2 +CO	vary	
39	FORM	= CO	vary	
40	FORM+O	= OH +HO2 +CO	237.	1550.
41	FORM+NO3	= HNO3 +HO2 +CO	0.93	
42	FROX+NO	= NO2 +HO2	10400.	
43	FROX	= FORM +HO2	90.	
44	ALD2+O	= C2O3 +OH	636.	986.
45	ALD2+OH	= C2O3	24000.	-250.

46	ALD2+NO3	= C2O3 +HNO3	3.7	
47	ALD2	= MEO2 +HO2 +CO	vary	
48	ALD2+HO2	= MEO2 +FORM	5.	
49	C2O3+NO	= MEO2 +NO2	16500.	-250.
50	C2O3+NO2	= PAN	9000.	-250.
51	PAN	= C2O3 +NO2	0.0222	14000.
52	MEO2+NO2	= MPNA	6000.	-735.
53	MPNA	= MEO2 +NO2	92.	10400.
54	MEO2+NO	= MEO +NO2	11000.	-180.
55	MEO +NO	= MNIT	44400.	-200.
56	MEO +NO	= FORM +HO2 +NO	1920.	
57	MEO +NO2	= MEN3	22200.	
58	MEO	= FORM +HO2	394000.	1313.
59	MEN3+OH	= FORM +NO2	2220.	360.
60	MNIT+OH	= FORM +NO	2370.	340.
61	MNIT	= MEO +NO	0.3 X k1	
62	MEO2+MEO2	= 0.70MEO +0.65FORM	503.	-220.
63	MEO2+C2O3	= MEO +MEO2	4400.	
64	C2O3+C2O3	= 2. MEO2	3700.	
65	MEO2+HO2	=	8900.	-1300.
66	C2O3+HO2	=	9600.	
67	AONE	= MEO2 +C2O3	0.0002 X k1	
68	AONE+OH	= XO2 +FORM +C2O3	580.	
69	GLY	= 1.79CO +0.21FORM + 0.19HO2	0.0075 X k1	
70	GLY +OH	= HO2 +2. CO	15000.	
71	MGLY	= C2O3 +HO2 +CO	0.02 X k1	
72	MGLY+OH	= XO2 +C2O3	26000.	
73	OH	= MEO2	21.	
74	PAR +OH	= 0.92XO2 +0.79ROR + 0.13HO2 +0.13ALD2 + -0.13PAR	1150.0	
75	ROR +NO2	=	22000.	
76	ROR	= 0.38KET +0.38HO2 + 0.62AONE +0.62D + -1.24PAR	390000.	
77	ROR	= ALD2 +D -PAR	90000.	7000.
78	D +PAR	= XO2 +HO2 +0.7AONE + 0.3ALD2 -1.7PAR	10000.	
79	D +KET	= C2O3 -PAR	10000.	
80	XO2 +NO	= NO2	12000.	
81	KET	= C2O3 +XO2 +HO2 +ALD2 + -3.0PAR	0.0003 X k1	
82	O +OLE	= 0.95ALD2 +0.30HO2 + 0.15XO2 +0.15CO + 0.05MEO2 +0.05C2O3 + -0.35PAR	5920.	324.
83	OH +OLE	= MEO2 +ALD2 -PAR	42000.	-537.
84	O3 +OLE	= 0.5ALD2 +0.516FORM + 0.3MCRG +0.3CRIG + 0.212CO +0.136HO2 + 0.144MEO2 -PAR	0.018	1897.

85	NO3 +OLE	= 0.91XO2 +0.91HO2	11.4	
86	O +ETH	= MEO2 +HO2 +CO	1080.	800.
87	OH +ETH	= MEO2 +FORM	12000.	-382.
88	O3 +ETH	= FORM +0.37CRIG + 0.37CO +0.13HO2	0.0027	2840.
89	CRIG+NO	= FORM +NO2	10000.	
90	CRIG+NO2	= FORM +NO3	1000.	
91	CRIG+H2O	=	.006	
92	CRIG+FORM	=	30.	
93	CRIG+ALD2	=	30.	
94	MCRG+NO	= ALD2 +NO2	10000.	
95	MCRG+NO2	= ALD2 +NO3	1000.	
96	MCRG+H2O	=	0.006	
97	MCRG+FORM	=	30.	
98	MCRG+ALD2	=	30.	
99	TOL +OH	= HO2 +0.64XO2 +1.13GLY + 0.56MGLY +0.36PHEN + 0.36PAR +0.08BZA	9750.	
100	PHEN+NO3	= PHO +HNO3	14000.	
101	BZA +OH	= BZO2	20000.	
102	BZO2+NO2	= PBZN	2500.	
103	BZO2+NO	= XO2 +PHO +CO	3700.	
104	PBZN	= BZO2 +NO2	0.022	14000.
105	BZA	=	0.004	
106	PHO +NO2	=	20000.	
107	XYL +OH	= HO2 +0.72XO2 +0.67GLY + 1.33MGLY +0.28PHEN + 0.56PAR +0.06TLA	36000.	
108	TLA +OH	= XO2 +PHO +2. PAR	20000.	
109	ISOP+O	= HO2 +0.8ALD2 +0.55OLE + 0.5XO2 +0.5CO +0.2KET + 0.45ETH -0.3PAR	28000.	
110	ISOP+OH	= ISO5	126000.	
111	ISOP+O3	= FORM +0.45ALD2 + 0.55ETH +0.98HO2 + 0.1OLE +0.2KET + 0.06CO -0.45PAR	0.018	
112	ISOP+NO3	= ISNT	165.	
113	ISNT+NO	=	10000.	
114	ISO5+NO	= 0.87NO2 +0.87FORM + 0.87HO2 +0.58KET 0.29OLE +0.58ETH 0.29ALD2 -0.29PAR	10000.	
115	ISO5+HO2	=	10000.	

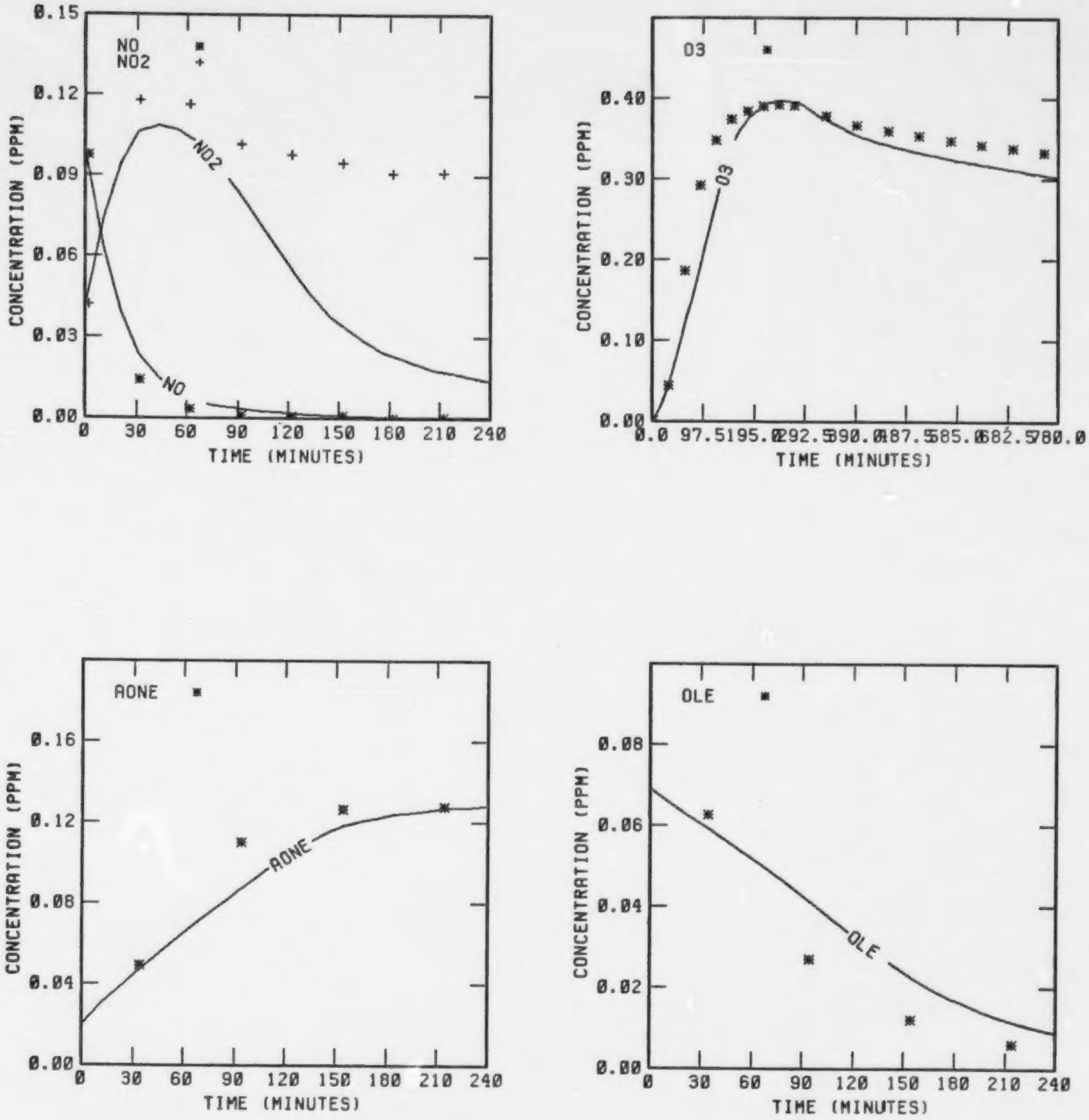

FIGURE 1a. SIMULATION RESULTS FOR
OTCB.101083 USING
THE CBM-RR

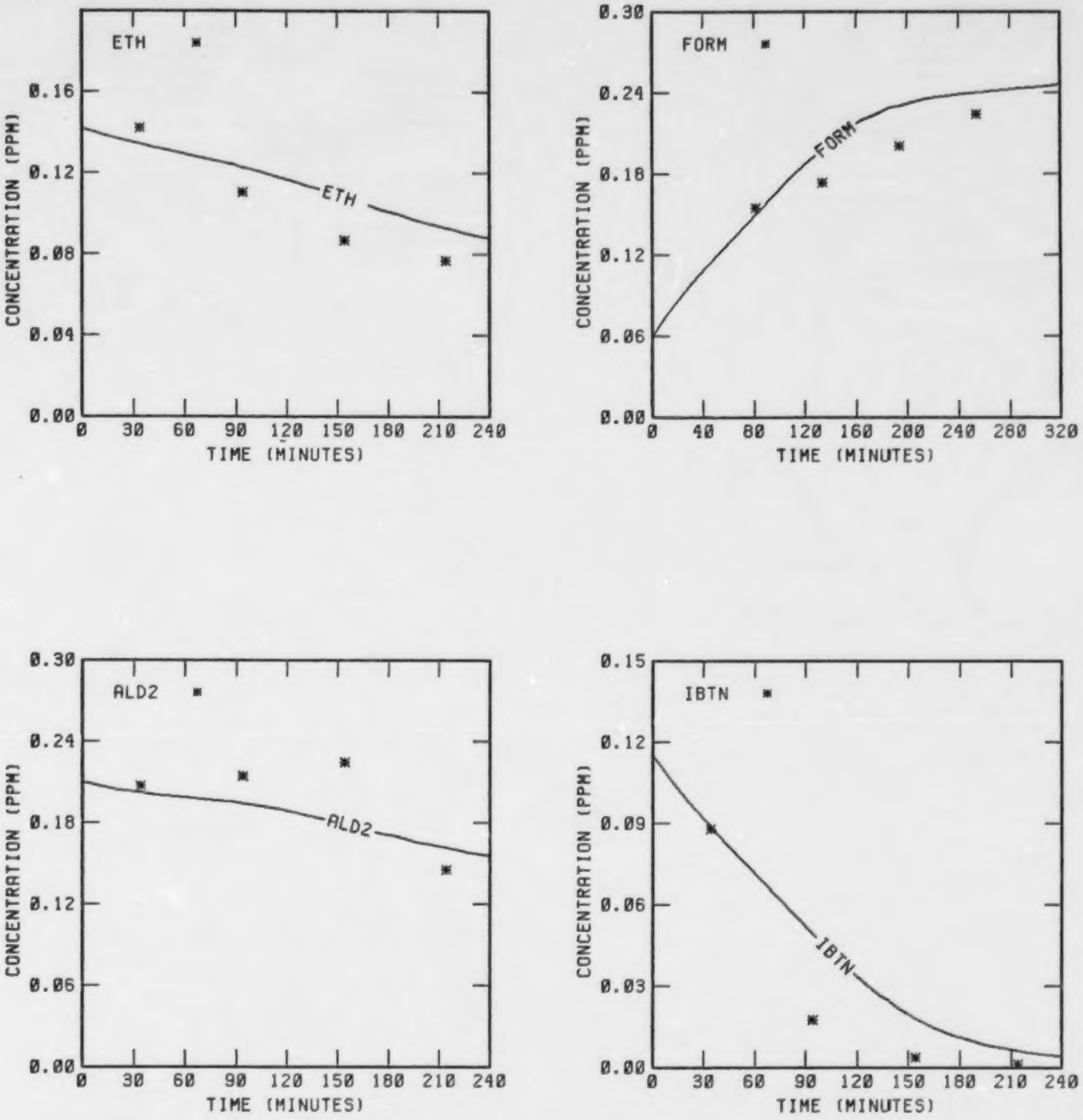

FIGURE 1a. SIMULATION RESULTS FOR
OTCB.101083 USING
THE CBM-RR
(continued).

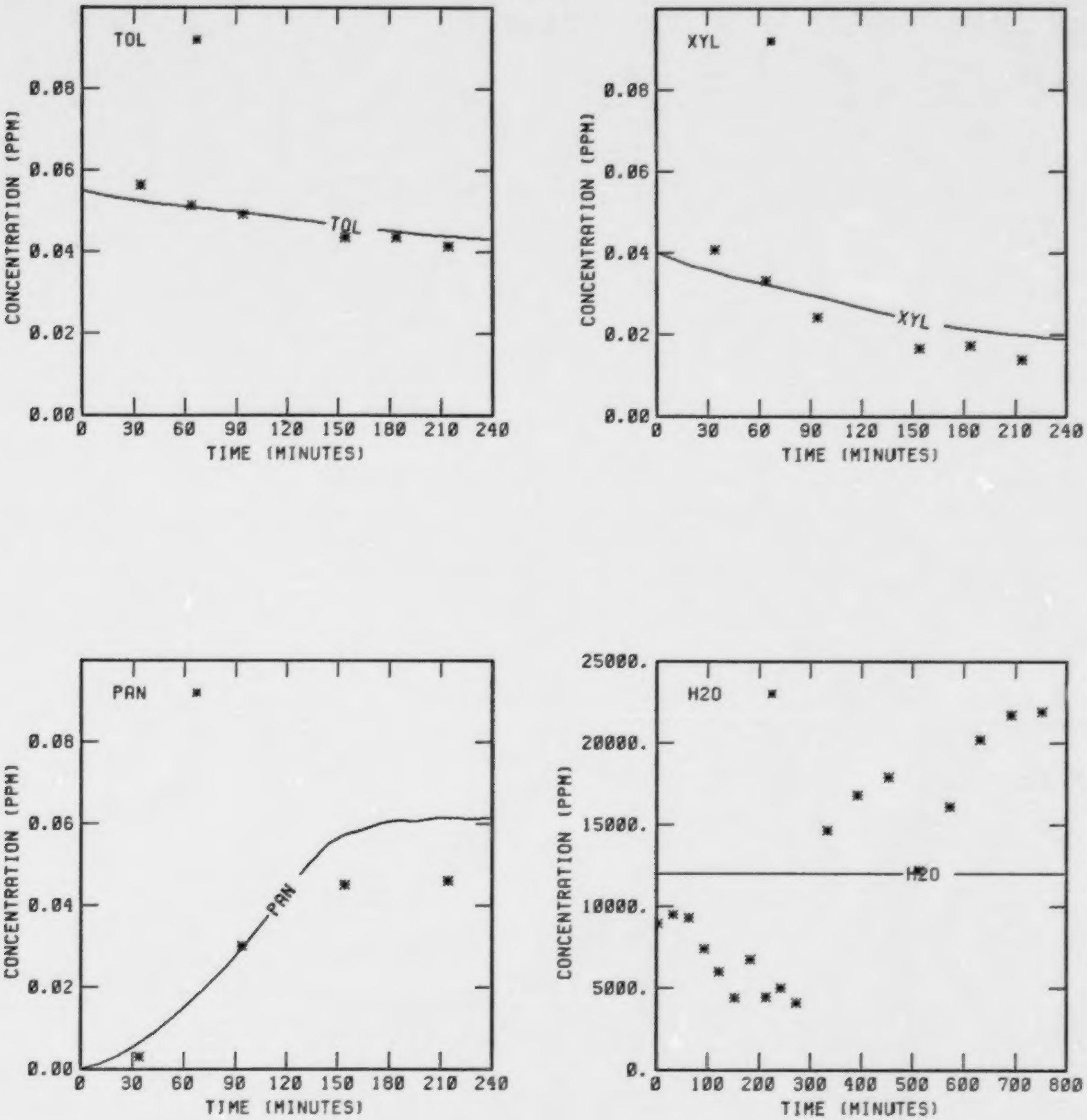

FIGURE 1a. SIMULATION RESULTS FOR
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THE CBM-RR
(continued).

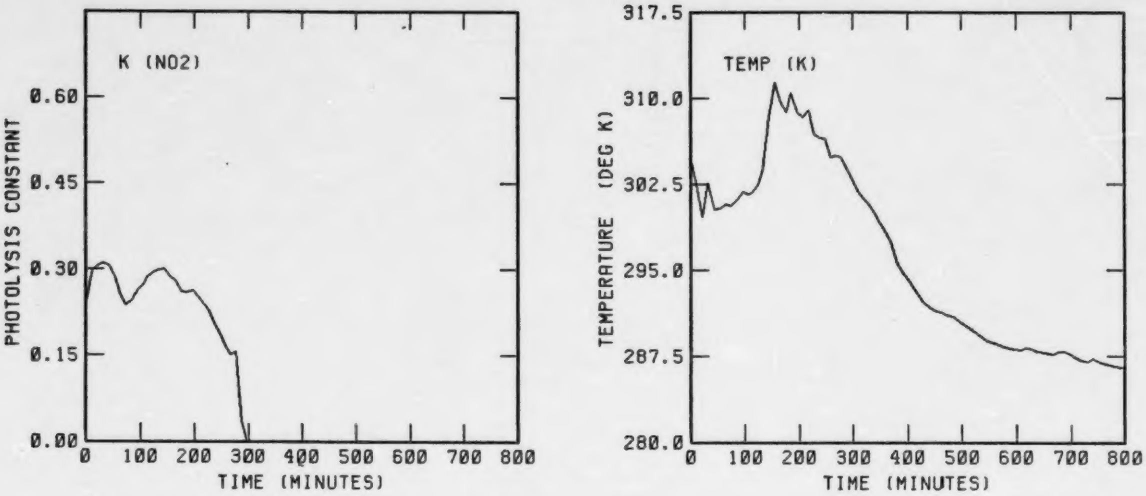

FIGURE 1a. SIMULATION RESULTS FOR
OTCB.101083 USING
THE CBM-RR
(concluded).

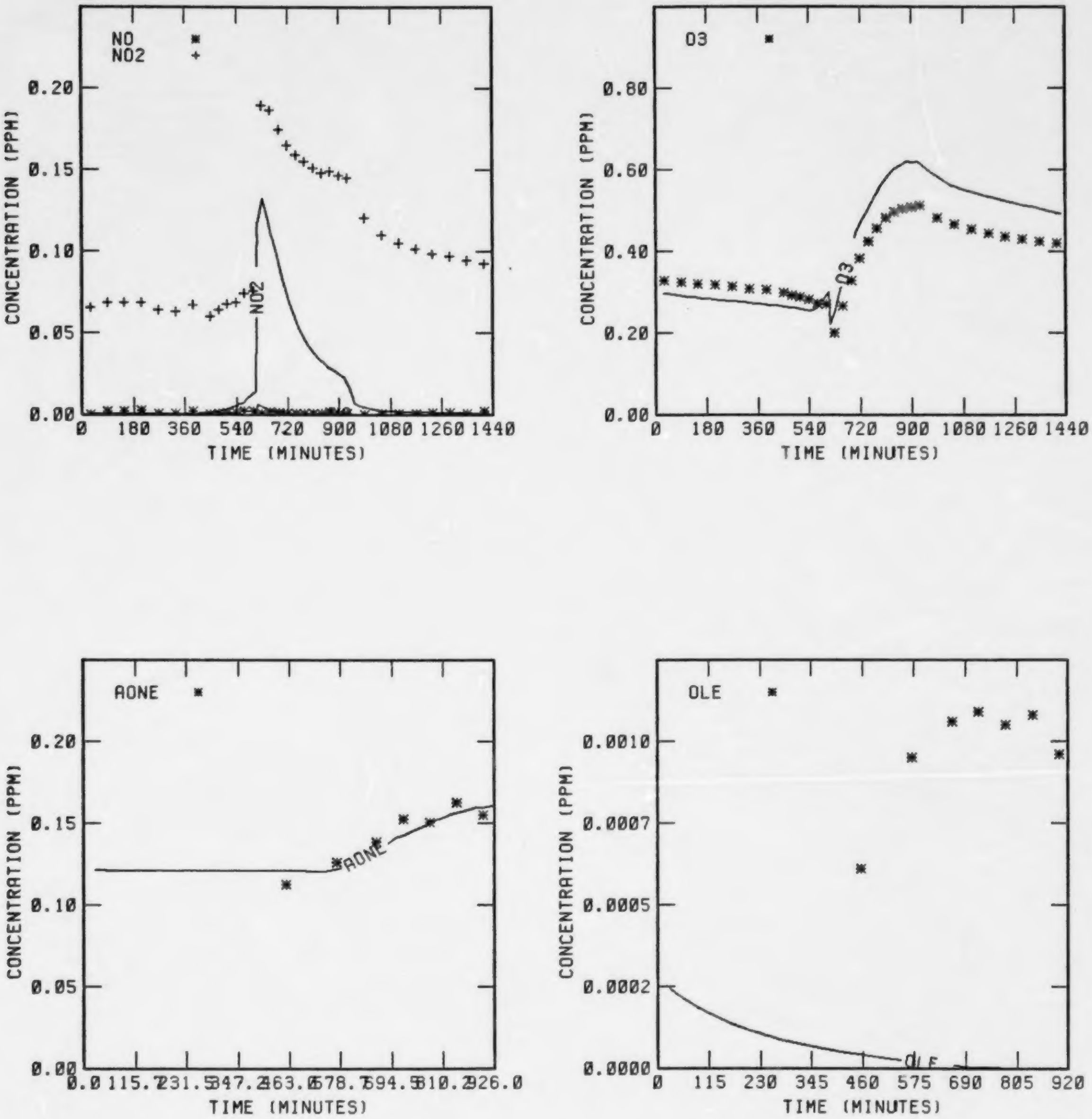

FIGURE . 1b. SIMULATION RESULTS FOR
OTCB.101183 USING
THE CBM- RR

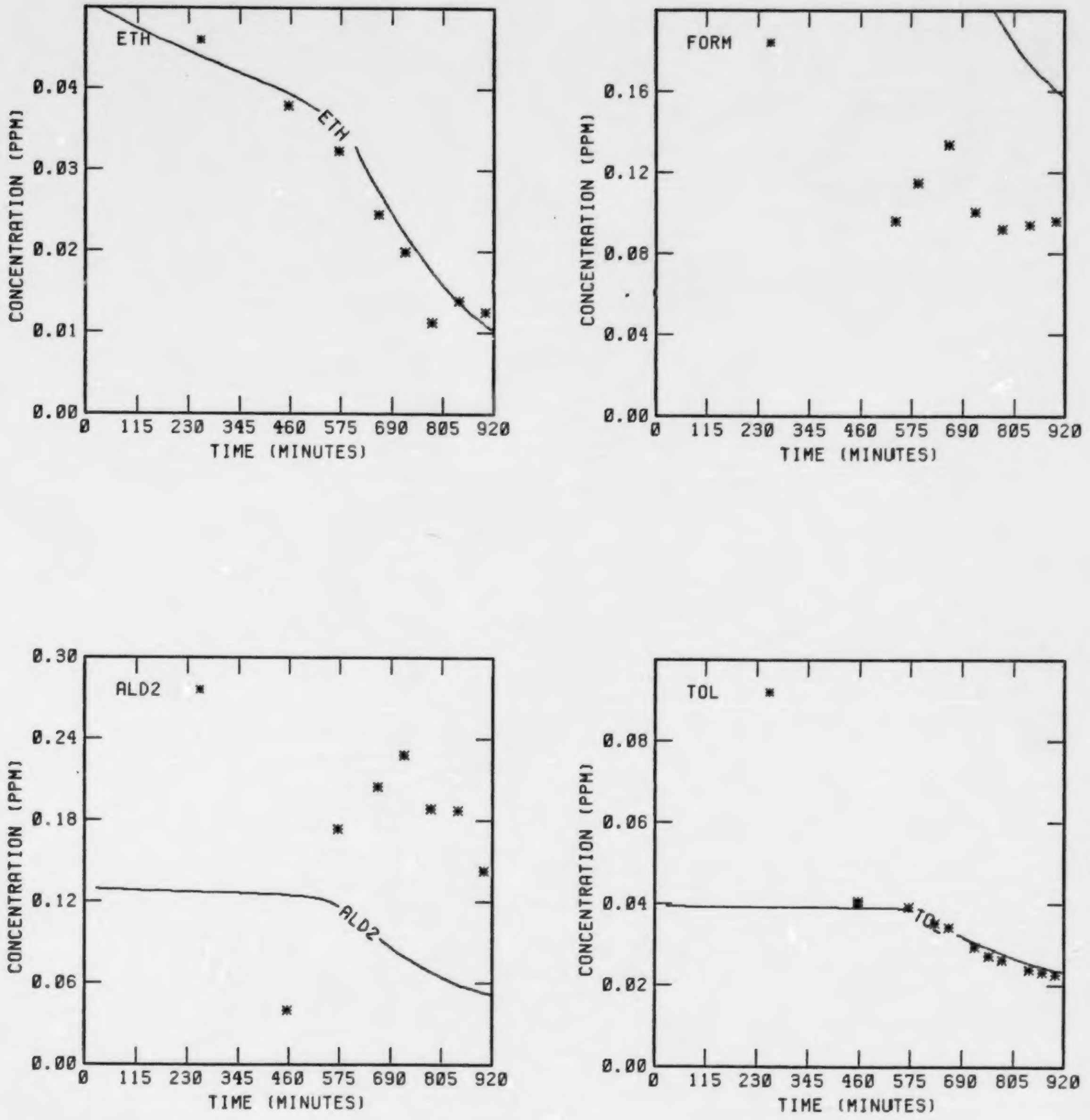

FIGURE 1b. SIMULATION RESULTS FOR
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THE CBM- RR
(continued).

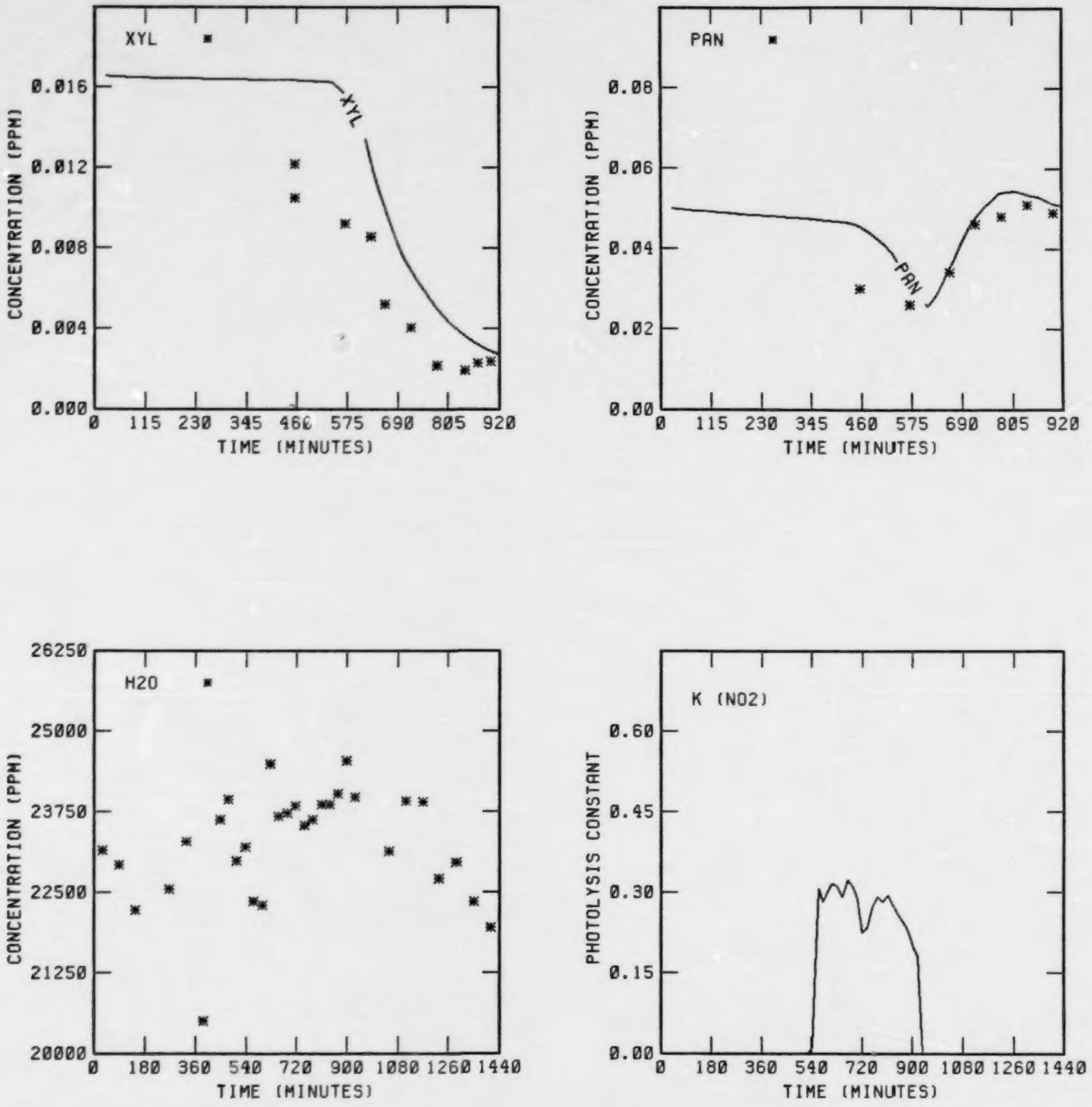

FIGURE 1b SIMULATION RESULTS FOR
OTCB.101183 USING
THE CBM-RR
(continued).

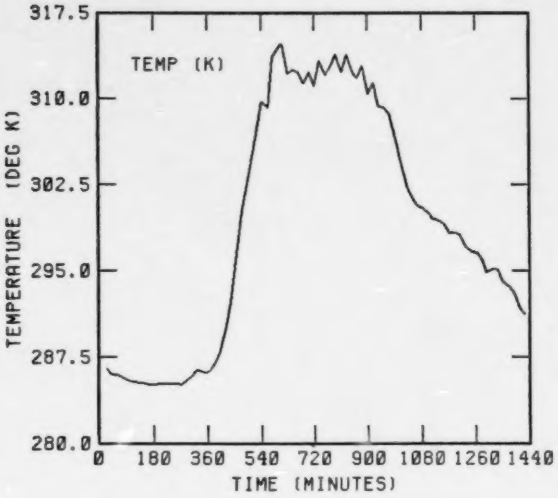

FIGURE 1b SIMULATION RESULTS FOR OTCB.101183 USING THE CBM- RR (concluded).

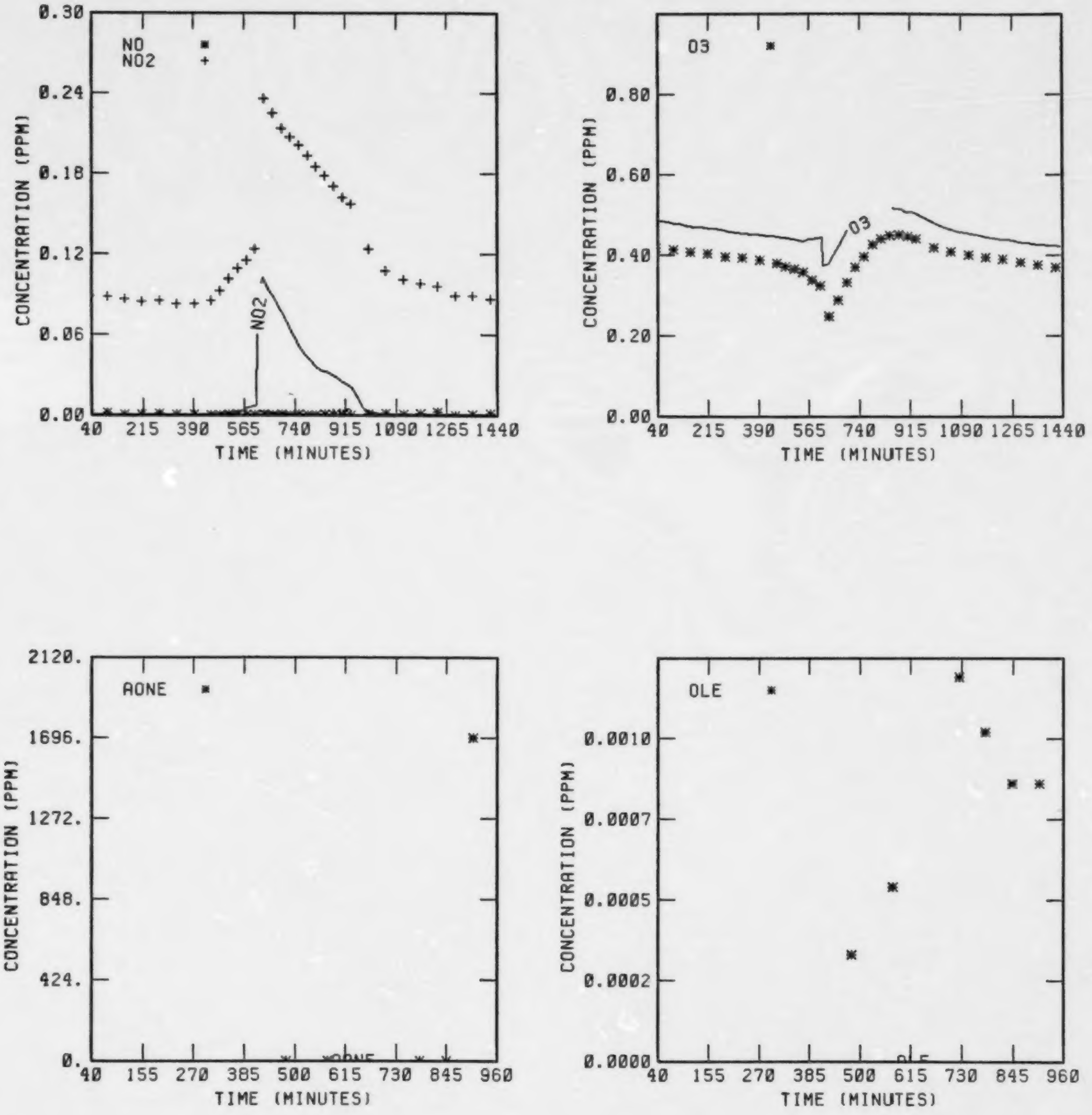

FIGURE 1c. SIMULATION RESULTS FOR
OTCB.101283 USING
THE CBM-RR

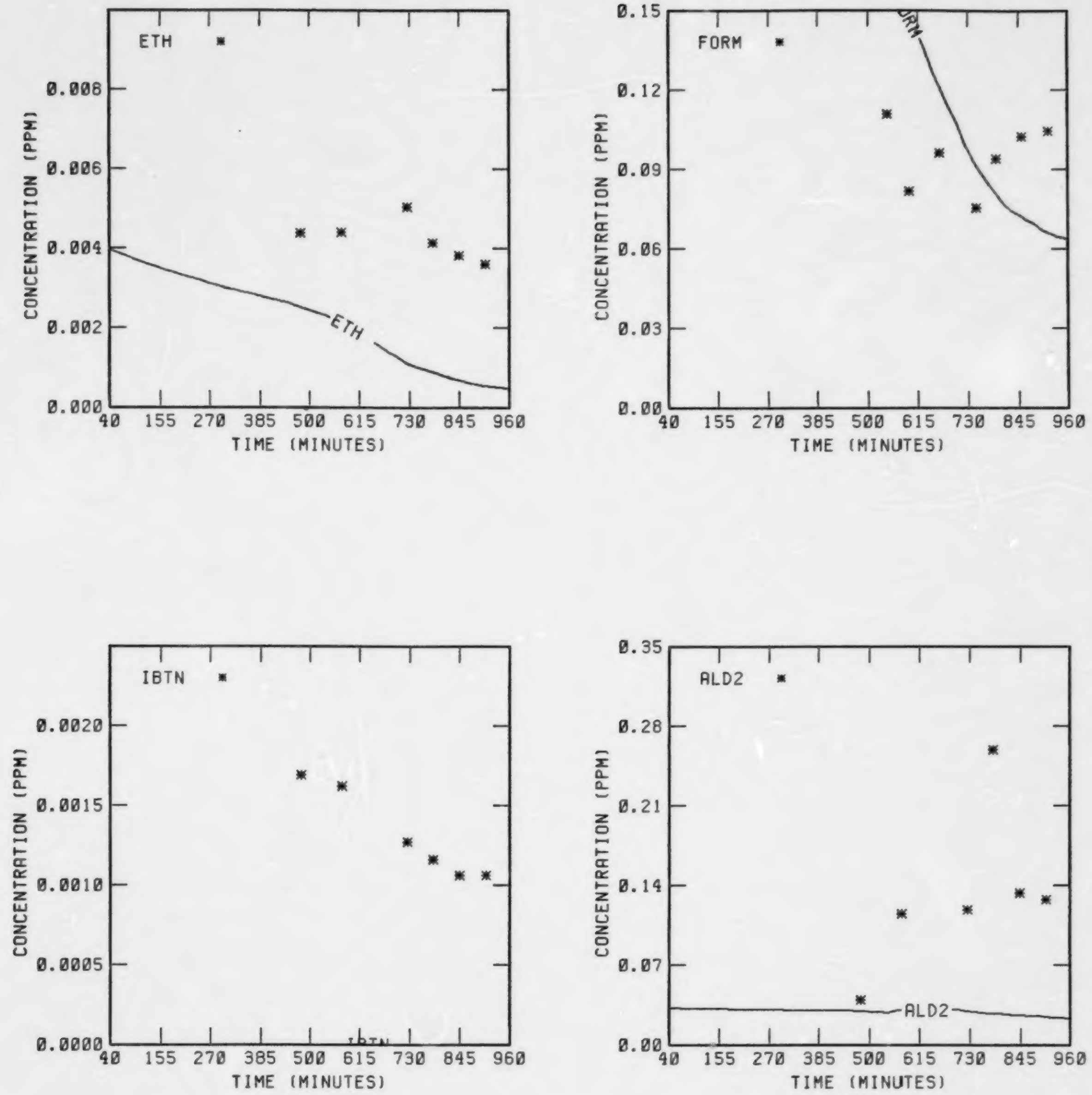

FIGURE 1c. SIMULATION RESULTS FOR
OTCB.101283 USING
THE CBM-RR
(continued).

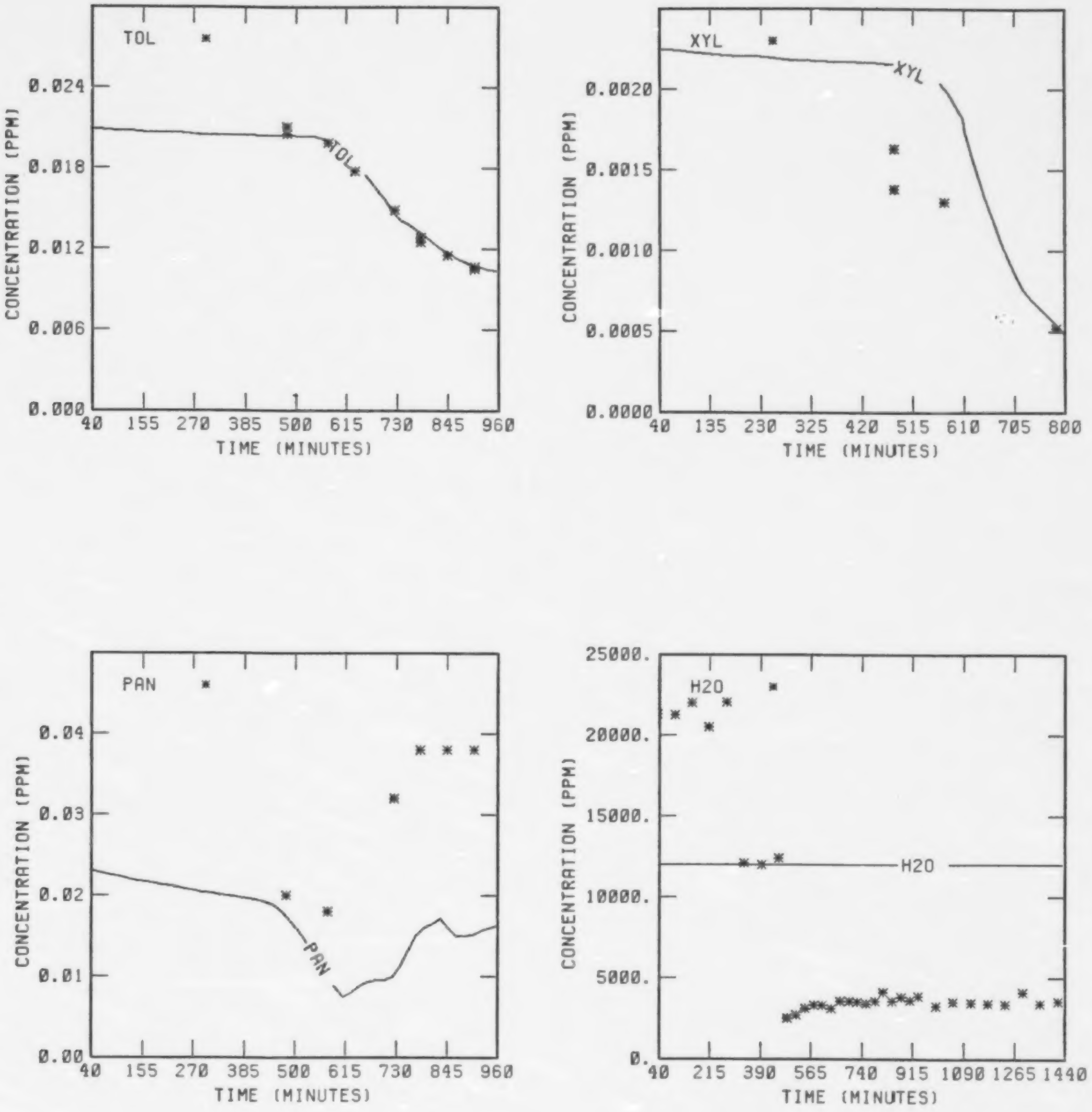

FIGURE 1c. SIMULATION RESULTS FOR
OTCB.101283 USING
THE CBM-RR
(continued).

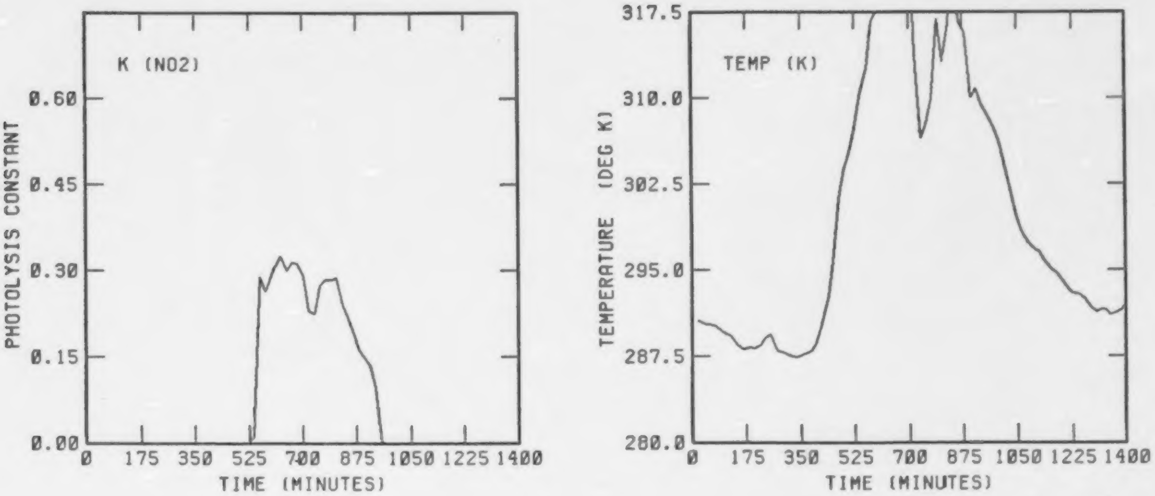

FIGURE 1c. SIMULATION RESULTS FOR
OTCB.101283 USING
THE CBM-RR
(concluded).

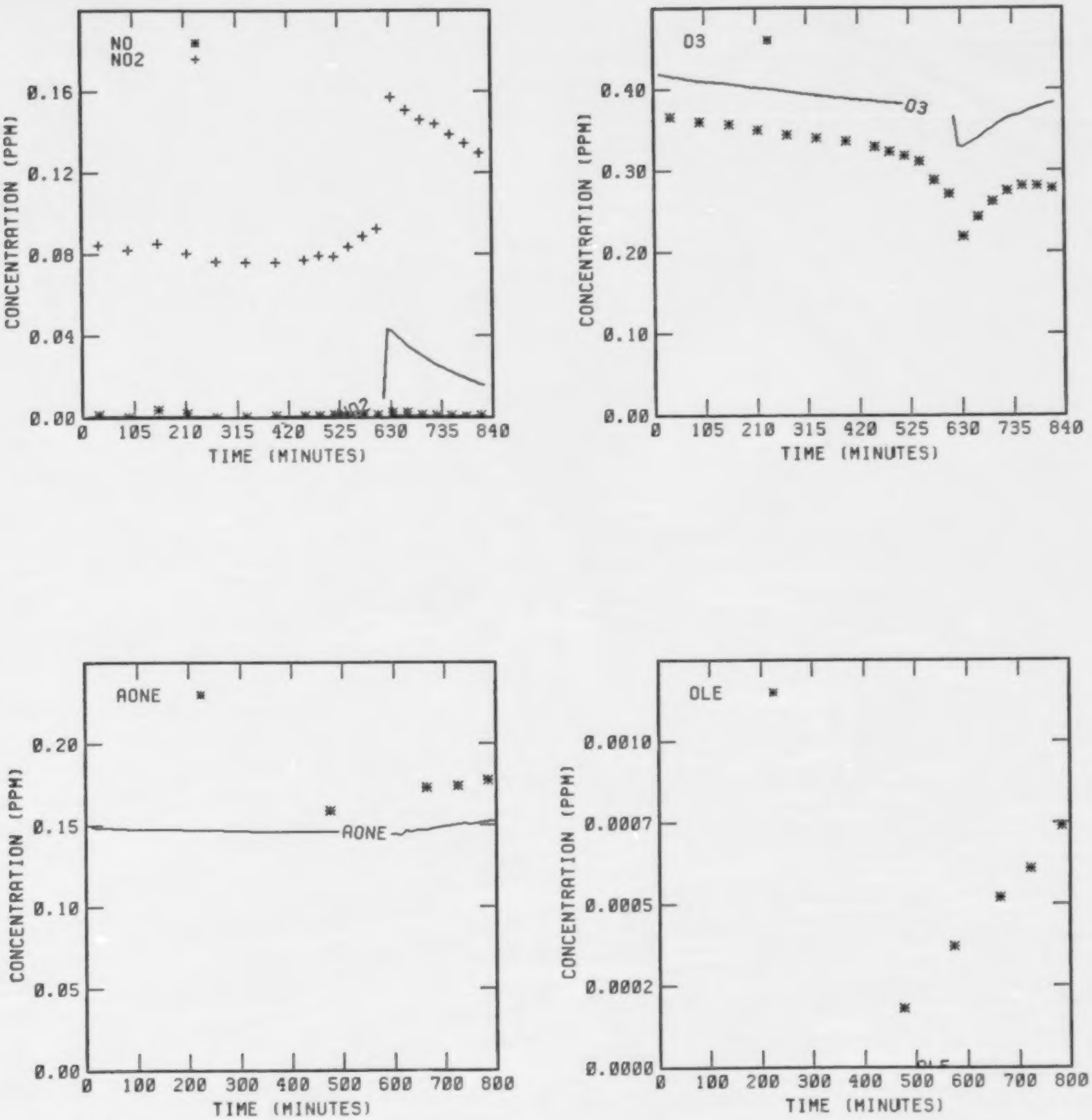

FIGURE 1d. SIMULATION RESULTS FOR
OTCB.101383 USING
THE CBM-RR

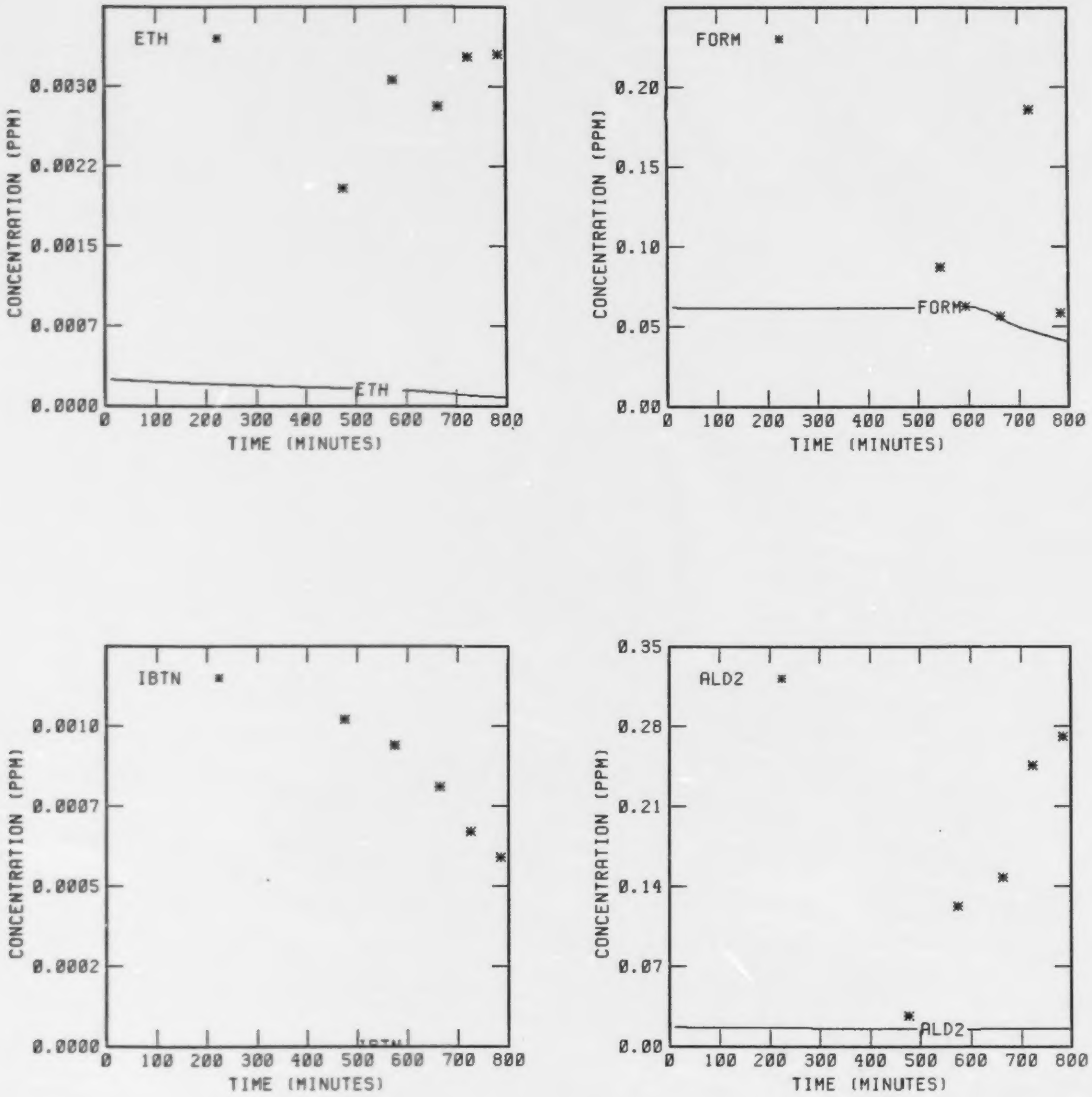

FIGURE 1d. SIMULATION RESULTS FOR OTCB.101383 USING THE CBM-RR (continued).

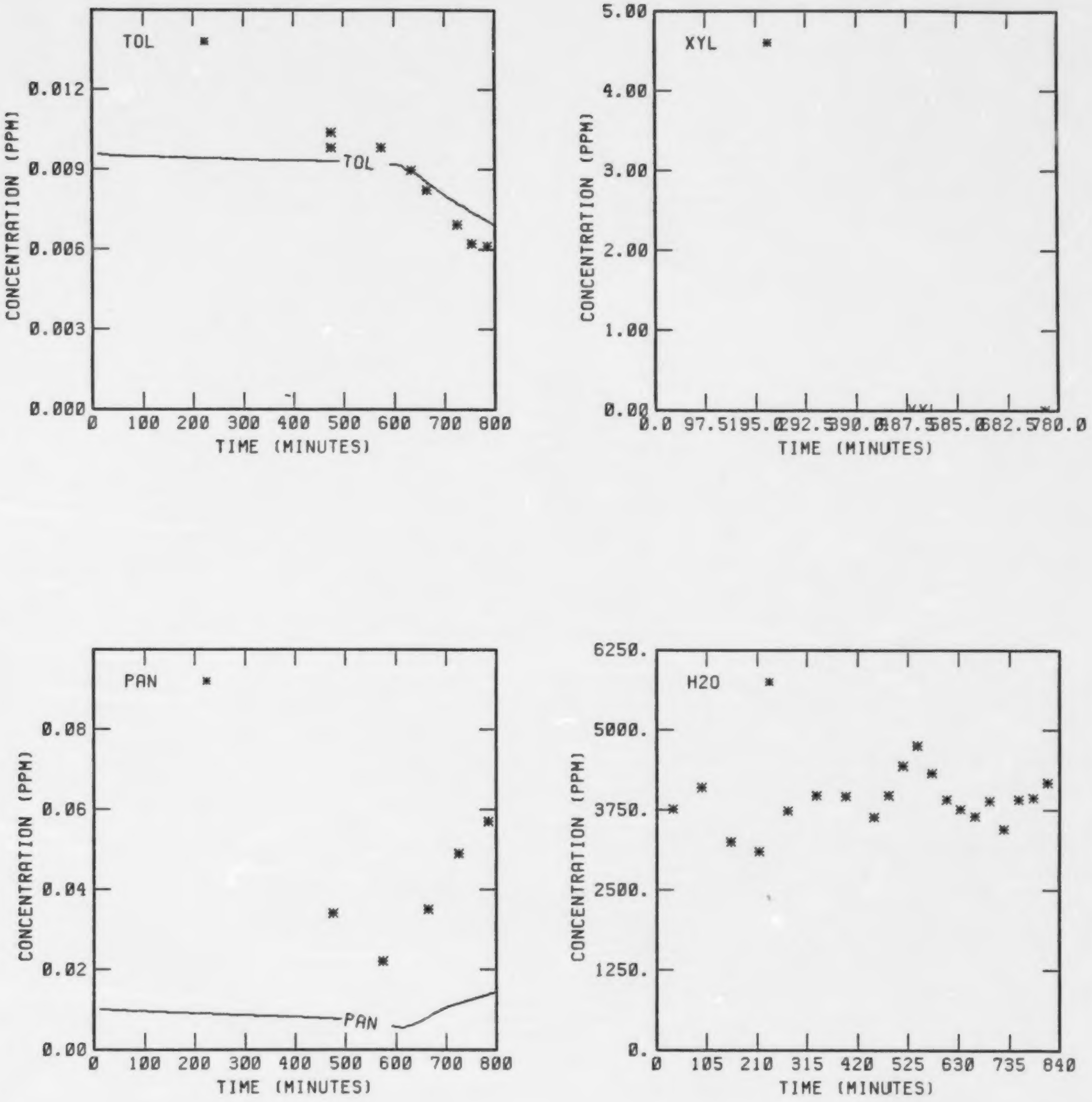

FIGURE 1d. SIMULATION RESULTS FOR
OTCB.101383 USING
THE CBM-RR
(continued).

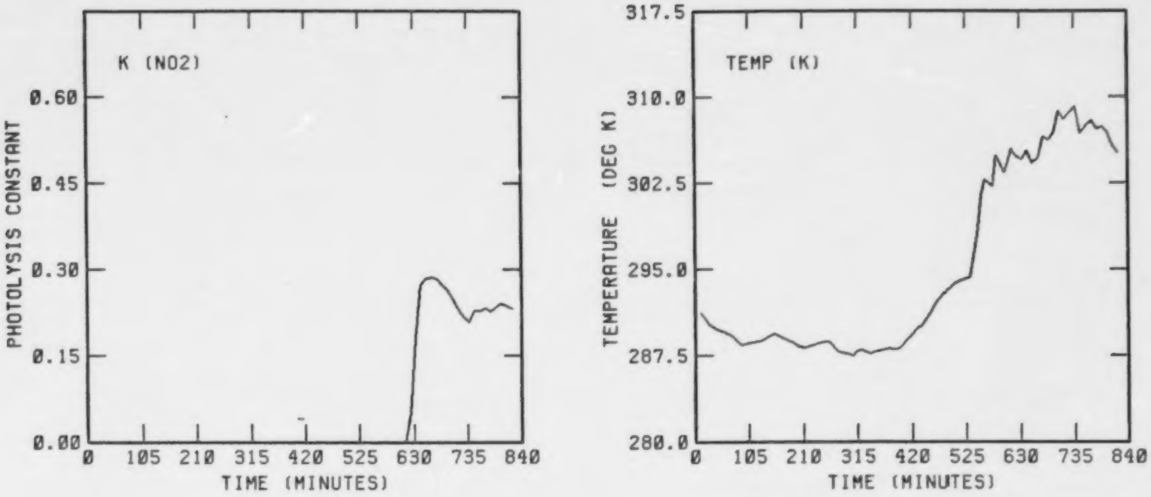

FIGURE 1d. SIMULATION RESULTS FOR OTCB.101383 USING THE CBM-RR (concluded).

SECTION 5

CONCLUSION

SUMMARY OF RESULTS

Two versions of a chemical kinetics mechanism for modeling regional oxidant formation have been developed. The first version, known as the Expanded Carbon-Bond Mechanism for Regional Modeling (CBM-XR), is written as a series of reactions with unit stoichiometric coefficients and no more than four products each. The second version, called the CBM-RR, is designed for use in computer coding where the number of species must be kept below 50. Although there is no substantial difference in the chemistry of the two mechanisms, the reduced version has only 47 species and 115 reactions whereas, the full CBM-XR has 78 species and 170 reactions.

The larger version (CBM-XR) is more easily described, modified, tested, and updated because it is composed of several subsets that clearly relate to known or evaluated chemical reactions. In the reduced version (CBM-RR) all unreactive (or untreated) products are removed, constant species are eliminated, fractional stoichiometric coefficients are used, and a generalized peroxy species is used in place of several special peroxy radicals. The resultant intricate array of fractional products used in the reactions causes a problem with modifying, testing, or updating the reduced CBM-RR. Although the fractional products were derived from the full CBM-XR using straightforward algebraic substitutions, it would be difficult to reverse the procedure and derive the CBM-XR product distribution from the CBM-RR mechanism. Nevertheless, the reduced form is a more appropriate mechanism for atmospheric models because computer costs can be substantially reduced by using fewer species.

The CBM-XR, as explained earlier, is a modification of the Expanded Carbon-Bond Mechanism (CBM-X) developed by Whitten, Killus, and Johnson (1985). The modification involved adding an organic subset of reactions to treat the natural hydrocarbon, isoprene, and expanding the validation data base to include multiday outdoor smog chamber experiments. The subset added to the CBM-X for isoprene was successfully tested against a series of isoprene experiments (as shown in Appendix B). The multiday tests, which are important to regional-scale oxidant formation (as shown in Appendix C), also successfully demonstrated the capability of the CBM-XR. The reduced form of the CBM-XR (the CBM-RR) was also shown to simulate atmospheric chemistry as well as the full mechanism does. Hence, the CBM-RR mechanism is appropriate for use in EPA's Regional Oxidant Model.

RECOMMENDATIONS FOR FUTURE STUDIES

The CBM-RR is still a very large and complex mechanism. Further testing of the full CBM-XR is recommended, with the goal of creating a series of condensed mechanisms that would eventually lead to a highly parameterized version of minimal size (10-15 reactions). At each stage of condensation, certain assumptions will have to be made to reduce the number of species and reactions. Depending on the assumptions made, some differences in simulation accuracy between the full CBM-XR and the condensed versions might result. At each stage of condensation, the resulting "costs" in accuracy will have to be balanced against the "savings" realized from the condensation.

There are a number of steps that could be taken to further condense the CBM-RR. The possibility of eliminating species involved in "do-nothing cycles" should be considered. Such candidate species for elimination include PNA, MPNA, MNIT, FROX, HNO2, PAN, and PBZN. However, the elimination of PAN is not recommended because it is an important oxidant and reservoir of NO_x and radicals. The criteria for elimination of each of these species should be similar to those used to determine the use of steady-state treatment. The forward and reverse reactions must be fast compared to the rate of change of the species and there must be no significant mass balance problems. PAN is an example of a species that in some circumstances does not meet all of these criteria. The species HNO_2 might also be a poor choice for elimination because HNO_2 has been observed to build up during nighttime periods (Harris et al., 1982; Killus and Whitten, 1985). Therefore, HNO_2 can act as a net source of radicals if emitted or formed by some pathway not using a radical. The species MNIT and FROX also have alternate pathways to be considered.

Another type of condensation for future study involves the removal of unimportant reactions and species. However, the choice of test simulations to document such condensations is sometimes difficult and uncertain. The regional oxidant model must be applied to multiday, urban, rural, and clean-air simulations, as well as to combinations of these conditions. In addition, it must be able to address the mixing of aged and fresh pollutants under these diverse same conditions; hence, one must ensure that the final condensed mechanism that is developed in the future performs as well as the original. The CBM-RR can be considered equivalent to the original CBM-XR mechanism because the steps introduced to condense the CBM-XR did not require "situation-dependent" assumptions (with the possible exception of the use of XO_2 as discussed earlier).

REFERENCES

Carter, W.P.L., M. C. Dodd, W. D. Long, and R. Atkinson. 1985. "Outdoor Chamber Study to Test Multi-Day Effects--Volume I: Results and Discussion." Final Report Cooperative Agreement, U.S. Environmental Protection Agency (CR810260-01).

Harris, G. W., W.P.L. Carter, A. M. Winer, and J. N. Pitts, Jr. Observations of nitrous acid in the Los Angeles atmosphere and implications for predictions of ozone-precursor relationships. Environ. Sci. Technol., 16:414-419.

Killus, J. P., and G. Z. Whitten. 1982. A mechanism describing the photochemical oxidation of toluene in smog. Atmos. Environ., 15(8):1973-1988.

Killus, J. P., and G. Z. Whitten. 1983. Discussion: Formation of chemical compounds from irradiated mixtures of aromatic hydrocarbons and nitrogen oxides. Atmos. Environ., 17:1597-1600.

Killus, J. P., and G. Z. Whitten. 1984a. Isoprene: A photochemical kinetic mechanism. Environ. Sci. Technol., 18:142-148.

Killus, J. P., and G. Z. Whitten. 1984b. "Technical Discussions Relating to the Use of the Carbon-Bond Mechanism in OZIPM/EKMA." U.S. Environmental Protection Agency, Research Triangle Park, North Carolina (EPA-450/4-84-009).

Killus, J. P., and G. Z. Whitten. 1985. Behavior of trace NO_x species in the nighttime urban atmosphere. J. Geophys. Res., 90:2430-2433.

Lamb, R. G. 1982. "A Regional Scale (1000 km) Model for Photochemical Air Pollution, Part 1, Theoretical Formulation," U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

Niki, H., P. P. Maker, C. M. Savage, and L. P. Breitenbach. 1981. An FTIR study of mechanisms for the HO radical initiated oxidation of C_2H_4 in the presence of NO: Detection of glycoladehyde. Chem. Phys. Lett., 80:499-503.

Reynolds, S. D., L. Reid, M. Hillyer, J. P. Killus, T. W. Tesche, R. I. Pollack, G. E. Anderson, and J. Ames. 1979. "Photochemical Modeling of Transportation Control Strategies--Volume I. Model Development, Performance Evaluation, and Strategy Assessment." Systems Applications, Inc., San Rafael, California (DOT-FH-11-8529).

Tuazon, E. C., R. Atkinson, H. MacLeod, H. W. Biermann, A. M. Winter, W.P.L. Carter, and J. N. Pitts, Jr. 1984. Yields of glyoxal and methylglyoxal from NO_x-Air Photooxidations of toluene and m- and p-Xylene. Environ. Sci. Technol., 18:981-984.

Whitten, G. Z. 1983. "The Chemistry of Smog Formation: A Review of Current Knowledge." Environ. Int., 9:447-463.

Whitten, G. Z., H. Hogo, and J. P. Killus. 1980. "The Carbon-Bond Mechanism: A Condensed Kinetic Mechanism for Photochemical Smog." Environ. Sci. Technol., 14:690-700.

Whitten, G. Z., J. P. Killus, and H. Hogo. 1979. "Modeling of Simulated Photochemical Smog with Kinetic Mechanisms." U.S. Environmental Protection Agency, Research Triangle Park, North Carolina (EPA-600/3-0012).

Whitten, G. Z., J. P. Killus, and R. G. Johnson. 1985. "Modeling of Auto Exhaust Smog Chamber Data for EKMA Development." U.S. Environmental Protection Agency, Research Triangle Park, North Carolina (68-02-3735).

Appendix A

DECOMPOSITION OF ORGANIC COMPONENTS IN TERMS OF THE CBM-XR FORMULATION

The carbon groups that are used to represent hydrocarbon molecules include OLE (double-bonded carbon atoms except ethene), PAR (single-bonded carbon atoms), TOL (toluene), XYL (xylene), FORM (formaldehyde), ALD2 (two-carbon atom carbonyl group), KET (ketone), ISOP (isoprene), ETH (ethene), and UNREAC (unreactive carbon).

The decomposition of organic compounds in terms of the CBM-XR formulation is presented in Table A-1. The carbon values for the bond groups listed in this table are given in Table A-2.

TABLE A-1. SPECIES PROFILES BY BOND GROUPS FOR ROM MECHANISM

SAROAD No.	Chemical Name	OLE	PAR	TOL	XYL	FORM	ALD2	KET	ETH	UNREAC	ISOP
43814	1,1,1-Trichloroethane	--	--	--	--	--	--	--	--	2	
43820	1,1,2-Trichloroethane	--	--	--	--	--	--	--	--	2	
43813	1,1-Dichloroethane	--	--	--	--	--	--	--	--	2	
45225	1,2,3-Trimethylbenzene	--	1	--	1	--	--	--	--	--	
45208	1,2,4-Trimethylbenzene	--	1	--	1	--	--	--	--	--	
45207	1,3,5-Trimethylbenzene	--	1	--	1	--	--	--	--	--	
43218	1,3-Butadiene	1	--	--	--	2	--	--	--	--	
46201	1,4-Dioxane	1	--	--	--	--	1	--	--	--	
43245	1-Hexene	1	4	--	--	--	--	--	--	--	
43224	1-Pentene	1	3	--	--	--	--	--	--	--	
43312	1,T-2-C-4-TM-Cyclopentane	--	6	--	--	--	1	--	--	--	
43296	2,2,3-Trimethylpentane	--	8	--	--	--	--	--	--	--	
43276	2,2,4-Trimethylpentane	--	8	--	--	--	--	--	--	--	
43299	2,2,5-Trimethylpentane	--	8	--	--	--	--	--	--	--	
43291	2,2-Dimethylbutane	--	6	--	--	--	--	--	--	--	
43280	2,3,3-Trimethylpentane	--	8	--	--	--	--	--	--	--	
43279	2,3,4-Trimethylpentane	--	8	--	--	--	--	--	--	--	
43234	2,3-Dimethly-1-Butene	1	4	--	--	--	--	--	--	--	
50001	2,3-Dimethylbutane	--	6	--	--	--	--	--	--	--	
43274	2,3-Dimethylpentane	--	7	--	--	--	--	--	--	--	
43277	2,4-Dimethylhexane	--	8	--	--	--	--	--	--	--	
43271	2,4-Dimethylpentane	--	7	--	--	--	--	--	--	--	
43278	2,5-Dimethylhexane	--	8	--	--	--	--	--	--	--	
43308	2-Butylethanol	--	6	--	--	--	--	--	--	--	
43311	2-Ethoxyethanol	--	2	--	--	--	1	--	--	--	
43452	2-Ethoxyethyl Acetate	--	4	--	--	--	1	--	--	--	
50002	2-Ethyl-1-Butene	--	4	--	--	1	--	1	--	--	
43310	2-Methoxyethanol	--	1	--	--	--	1-	--	--	--	
43451	Isobutyl Isobutyrate	--	7	--	--	--	1	--	--	1	
43215	Isobutylene	--	1	--	--	1	1	--	--	--	

TABLE A-1 (continued)

SAROAD No.	Chemical Name	OLE	PAR	TOL	XYL	FORM	ALD2	KET	ETH	UNREAC	ISOP
43120	Isomers of Butene	--	--	--	--	--	2	--	--	--	
45105	Isomers of Butylbenzene	--	3	1	--	--	--	--	--	--	
43109	Isomers of Decane	--	10	--	--	--	--	--	--	--	
45106	Isomers of Diethylbenzene	--	2	--	1	--	--	--	--	--	
43112	Isomers of Dodecane	--	12	--	--	--	--	--	--	--	
45104	Isomers of Ethyltoluene	--	1	--	1	--	--	--	--	--	
43106	Isomers of Heptane	--	7	--	--	--	--	--	--	--	
43105	Isomers of Hexane	--	6	--	--	--	--	--	--	--	
45234	Isomers of Methylprop. Benzene	--	2	--	1	--	--	--	--	--	
43108	Isomers of Nonane	--	9	--	--	--	--	--	--	--	
43107	Isomers of Octane	--	8	--	--	--	--	--	--	--	
43114	Isomers of Pentadecane	--	15	--	--	--	--	--	--	--	
43122	Isomers of Pentane	--	5	--	--	--	--	--	--	--	
43121	Isomers of Pentene	--	1	--	--	--	2	--	--	--	
45108	Isomers of Propylbenzene	--	2	1	--	--	--	--	--	--	
43113	Isomers of Tetradecane	--	14	--	--	--	--	--	--	--	
43111	Isomers of Tridecane	--	13	--	--	--	--	--	--	--	
45107	Isomers of Trimethylbenzene	--	1	--	1	--	--	--	--	--	
43110	Isomers of Undecane	--	11	--	--	--	--	--	--	--	
45102	Isomers of Xylene	--	--	--	1	--	--	--	--	--	
43243	Isoprene	--	1	--	--	--	--	--	--	--	1
43444	Isopropyl Acetate	--	5	--	--	--	--	--	--	--	
43119	Lactol Spirits	--	8	--	--	--	--	--	--	--	
50022	m-Cresol (3-Methylbenzenol)	--	--	1	--	--	--	--	--	--	
45212	m-Ethyltoluene	--	1	--	1	--	--	--	--	--	
45205	m-Xylene	--	--	--	1	--	--	--	--	--	
43201	Methane	--	--	--	--	--	--	--	--	1	
43432	Methyl Acetate	--	--	--	--	--	--	--	--	3	
43229	2-Methyl Pentane	--	6	--	--	--	--	--	--	--	
43225	2-Methyl-1-Butene	1	3	--	--	--	--	--	--	--	

TABLE A-1 (continued)

SAROAD No.	Chemical Name	OLE	PAR	TOL	XYL	FORM	ALD2	KET	ETH	UNREAC	ISOP
43228	2-Methyl-2-Butene	--	3	--	--	--	1	--	--	--	
50004	2-Methyl-2-Pentene	--	4	--	--	--	1	--	--	--	
43275	2-Methylhexane	--	7	--	--	--	--	--	--	--	
43230	3-Methyl Pentane	--	6	--	--	--	--	--	--	--	
43223	3-Methyl-1-Butene	1	3	--	--	--	--	--	--	--	
43211	3-Methyl-1-Pentene	1	4	--	--	--	--	--	--	--	
43270	3-Methyl-T-2-Pentene	--	3	--	--	--	1	1	--	--	
43298	3-Methylheptane	--	8	--	--	--	--	--	--	--	
43295	3-Methylhexane	--	7	--	--	--	--	--	--	--	
43293	4-Methyl-T-2-Pentene	--	2	--	--	--	2	--	--	--	
43297	4-Methylheptane	--	8	--	--	--	--	--	--	--	
45221	A-Methylstyrene	--	--	1	--	1	--	--	--	--	
50025	A-Pinene	1	8	--	--	--	--	--	--	--	
43503	Acetaldehyde	--	--	--	--	--	1	--	--	--	
43404	Acetic Acid	--	1	--	--	--	--	--	--	1	
43551	Acetone	--	3	--	--	--	--	--	--	--	
43702	Acetonitrile	--	1	--	--	--	--	--	--	1	
43206	Acetylene	--	1	--	--	--	--	--	--	1	
43704	Acrylonitrile	1	1	--	--	--	--	--	--	--	
50015	Anthracene	--	6	--	1	--	--	--	--	--	
50020	B-Methylstyrene	--	--	1	--	--	1	--	--	--	
50026	B-Pinene	1	8	--	--	--	--	--	--	--	
45201	Benzene	--	1	--	--	--	--	--	--	5	
50024	Benzylchloride	--	--	1	--	--	--	--	--	--	
43213	Butene	1	2	--	--	--	--	--	--	--	
43510	Butyraldehyde	--	2	--	--	--	1	--	--	--	
50003	C-3-Hexene	1	4	--	--	--	--	--	--	--	
43115	C-7 Cycloparaffins	--	7	--	--	--	--	--	--	--	
43116	C-8 Cycloparaffins	--	8	--	--	--	--	--	--	--	
43117	C-9 Cycloparaffins	--	9	--	--	--	--	--	--	--	

TABLE A-1 (continued)

SAROAD No.	Chemical Name	OLE	PAR	TOL	XYL	FORM	ALD2	KET	ETH	UNREAC	ISOP
43511	C3 Aldehyde	--	1	--	--	--	1	--	--	--	
43512	C5 Aldehyde	--	3	--	--	--	1	--	--	--	
43289	C6 Olefins	1	4	--	--	--	--	--	--	--	
43294	C7 Olefins	1	5	--	--	--	--	--	--	--	
43513	C8 Aldehyde	--	6	--	--	--	1	--	--	--	
43290	C8 Olefins	1	6	--	--	--	--	--	--	--	
43807	Carbon Tetrabromide	--	--	--	--	--	--	--	--	1	
43804	Carbon Tetrachloride	--	--	--	--	--	--	--	--	1	
43443	Cellosolve Acetate	--	3	--	--	--	1	--	--	1	
43803	Chloroform	--	--	--	--	--	--	--	--	1	
43217	Cis-2-Butene	--	--	--	--	--	2	--	--	--	
43227	Cis-2-Pentene	--	1	--	--	--	2	--	--	--	
50019	Cryofluorane (Freon 114)	--	--	--	--	--	--	--	--	2	
43248	Cyclohexane	--	6	--	--	--	--	--	--	--	
43264	Cyclohexanone	--	5	--	--	--	--	1	--	--	
43273	Cyclohexene	1	4	--	--	--	--	--	--	--	
43242	Cyclopentane	--	5	--	--	--	--	--	--	--	
43292	Cyclopentene	1	3	--	--	--	--	--	--	--	
43207	Cyclopropane	--	3	--	--	--	--	--	--	--	
50027	D-Limonene	1	4	--	--	--	2	--	--	--	
43320	Diacetone Alcohol	--	4	--	--	--	1	--	--	--	
43823	Dichlorodifluoromethane	--	--	--	--	--	--	--	--	1	
43802	Dichloromethane	--	--	--	--	--	--	--	--	1	
50018	Dimethyl Ether	--	2	--	--	--	--	--	--	--	
43450	Dimethyl Formamide	--	--	--	--	--	--	--	--	3	
50017	Dimethyl-2,3,Dihydro-1H-Indene	--	3	--	1	--	--	--	--	--	
45103	Dimethylethylbenzene	--	4	--	1	--	--	--	--	--	
50012	Dimethylnaphthalene	--	6	--	1	--	--	--	--	--	
43287	Docosane	--	22	--	--	--	--	--	--	--	
43285	Eicosane	--	20	--	--	--	--	--	--	--	

TABLE A-1 (continued)

SAROAD No.	Chemical Name	OLE	PAR	TOL	XYL	FORM	ALD2	KET	ETH	UNREAC	ISOP
43202	Ethane	--	.4	--	--	--	--	--	--	1.6	
43433	Ethyl Acetate	--	3	--	--	--	--	--	--	1	
43438	Ethyl Acrylate	--	1	--	--	--	2	--	--	--	
43302	Ethyl Alcohol	--	2	--	--	--	--	--	--	--	
43812	Ethyl Chloride	--	--	--	--	--	--	--	--	2	
43351	Ethyl Ether	--	2	--	--	--	1	--	--	--	
43219	Ethylacetylene	--	4	--	--	--	--	--	--	--	
43721	Ethylamine	--	1	--	--	--	--	--	--	1	
45203	Ethylbenzene	--	1	1	--	--	--	--	--	--	
43288	Ethylcyclohexane	--	8	--	--	--	--	--	--	--	
43203	Ethylene	--	--	--	--	--	--	--	1	--	
43815	Ethylene Dichloride	--	--	--	--	--	--	--	1	--	
43370	Ethylene Glycol	--	2	--	--	--	--	--	--	--	
43601	Ethylene Oxide	--	1	--	--	--	--	--	--	1	
50011	Ethylnaphthalene	--	5	1	--	--	--	--	--	--	
43502	Formaldehyde	--	--	--	--	1	--	--	--	--	
43368	Glycol	--	2	--	--	--	--	--	--	--	
43367	Glycol Ether	--	2	--	--	--	--	--	--	--	
43286	Heneicosane	--	21	--	--	--	--	--	--	--	
43282	Heptadecane	--	17	--	--	--	--	--	--	--	
43232	Heptane	--	7	--	--	--	--	--	--	--	
50005	Heptene	1	5	--	--	--	--	--	--	--	
43281	Hexadecane	--	16	--	--	--	--	--	--	--	
43231	Hexane	--	6	--	--	--	--	--	--	--	
43214	Isobutane	--	4	--	--	--	--	--	--	--	
43306	Isobutyl Alcohol	--	4	--	--	--	--	--	--	--	
43304	Isopropyl Alcohol	--	3	--	--	--	--	--	--	--	
43446	Isobutyl Acetate	--	6	--	--	--	--	--	--	--	
43301	Methyl Alcohol	--	1	--	--	--	--	--	--	--	
43445	Methyl Amyl Acetate	--	8	--	--	--	--	--	--	--	

TABLE A-1 (continued)

SAROAD No.	Chemical Name	OLE	PAR	TOL	XYL	FORM	ALD2	KET	ETH	UNREAC	ISOP
43801	Methyl Chloride	--	--	--	--	--	--	--	--	1	
43552	Methyl Ethyl Ketone	--	3	--	--	--	--	1	--	--	
43560	Methyl Isobutyl Ketone	--	5	--	--	--	--	1	--	--	
43559	Methyl N-Butyl Ketone	--	5	--	--	--	--	1	--	--	
43209	Methylacetylene	--	1.5	--	--	--	--	--	--	1.5	
50016	Methylanthracene	--	9	--	1	--	--	--	--	--	
43261	Methylcyclohexane	--	7	--	--	--	--	--	--	--	
43262	Methylcyclopentane	--	6	--	--	--	--	--	--	--	
43272	Methylcyclopentene	1	4	--	--	--	--	--	--	--	
43819	Methylene Bromide	--	--	--	--	--	--	--	--	1	
50010	Methylnaphthalene	--	5	--	1	--	--	--	--	--	
43118	Mineral Spirits	--	6	--	--	--	1	--	--	--	
45801	Monochlorobenzene	--	5	--	--	--	--	--	--	1	
43212	N-Butane	--	4	--	--	--	--	--	--	--	
43435	N-Butyl Acetate	--	5	--	--	--	--	--	--	1	
43305	N-Butyl Alcohol	--	2	--	--	--	1	--	--	--	
43238	N-Decane	--	10	--	--	--	--	--	--	--	
43255	N-Dodecane	--	12	--	--	--	--	--	--	--	
43260	N-Pentadecane	--	15	--	--	--	--	--	--	--	
43220	N-Pentane	--	5	--	--	--	--	--	--	--	
43303	N-Propyl Alcohol	--	3	--	--	--	--	--	--	--	
45209	N-Propylbenzene	--	2	1	--	--	--	--	--	--	
43259	N-Tetradecane	--	14	--	--	--	--	--	--	--	
43258	N-Tridecane	--	13	--	--	--	--	--	--	--	
45101	Naphtha	--	8	--	--	--	--	--	--	--	
43284	Nonadecane	--	19	--	--	--	--	--	--	--	
43235	Nonane	--	9	--	--	--	--	--	--	--	
50021	O-Cresol (2-Methylbenzenol)	--	--	1	--	--	--	--	--	--	
45211	O-Ethyltoluene	--	1	--	1	--	--	--	--	--	
45204	O-Xylene	--	--	--	1	--	--	--	--	--	

TABLE A-1 (continued)

SAROAD No.	Chemical Name	OLE	PAR	TOL	XYL	FORM	ALD2	KET	ETH	UNREAC	ISOP
43283	Octadecane	--	18	--	--	--	--	--	--	--	
43233	Octane	--	8	--	--	--	--	--	--	--	
43265	Octene	1	6	--	--	--	--	--	--	--	
50023	P-Cresol (4-Methylbenzenol)	--	--	1	--	--	--	--	--	--	
45206	P-Xylene	--	--	--	1	--	--	--	--	--	
43817	Perchloroethylene	--	--	--	--	--	--	--	--	2	
45300	Phenols	--	--	--	--	--	1	--	--	4	
50006	Propadiene	--	--	--	--	1	1	--	--	--	
43204	Propane	--	1.5	--	--	--	--	--	--	1.5	
43504	Proprionaldehyde	--	1	--	--	--	1	--	--	--	
43434	Propyl Acetate	--	4	--	--	--	--	--	--	1	
43205	Propylene	1	1	--	--	--	--	--	--	--	
43369	Propylene Glycol	--	3	--	--	--	--	--	--	--	
43602	Propylene Oxide	--	2	--	--	--	--	--	--	1	
50013	Propylnaphthalene	--	6	1	--	--	--	--	--	--	
43208	Propyne	--	2	--	--	--	--	--	--	1	
45216	Sec-Butylbenzene	--	3	1	--	--	--	--	--	--	
45220	Styrene	--	--	1	--	1	--	--	--	--	
43123	Terpenes	1	8	--	--	--	--	--	--	--	
43309	Tert-Butyl Alcohol	--	--	--	--	--	--	--	--	4	
45215	Tert-Butylbenzene	--	--	1	--	--	--	--	--	3	
43390	Tetrahydrofuran	--	3	--	--	1	--	--	--	--	
45232	Tetramethylbenzene	--	2	--	1	--	--	--	--	--	
45202	Toluene	--	--	1	--	--	--	--	--	--	
43216	Trans-2-Butene	--	--	--	--	--	2	--	--	--	
43226	Trans-2-Pentene	--	1	--	--	--	2	--	--	--	
45233	Tri/Tetraalkyl Benzene	--	3	--	1	--	--	--	--	--	
43824	Trichloroethylene	--	--	--	--	--	--	--	1	--	
43811	Trichlorofluoromethane	--	--	--	--	--	--	--	--	1	
43821	Trichlorotrifluoroethane	--	--	--	--	--	--	--	--	2	

TABLE A-1 (concluded)

SAROAD No.	Chemical Name	OLE	PAR	TOL	XYL	FORM	ALD2	KET	ETH	UNREAC	ISOP
43740	Trimethyl Amine	--	3	--	--	--	--	--	--	--	
43822	Trimethylfluorosilane	--	--	--	--	--	--	--	--	3	
50014	Trimethylnaphthalene	--	5	--	1	--	--	--	--	--	
43241	Undecane	--	11	--	--	--	--	--	--	--	
43860	Vinyl Chloride	--	--	--	--	--	--	--	1	--	
45401	Xylene Base Acids	--	--	--	1	--	--	--	--	--	

TABLE A-2. Carbon values for bond groups listed in Table A-1.

CBM-XR Group	Carbon Number
PAR	1
OLE	2
ETH	2
TOL	7
XYL	8
FORM	1
ALD2	2
ALD	1
KET	1
UNREAC	1
ISOP	4

Appendix B

SIMULATION RESULTS FOR THE UNC ISOPRENE EXPERIMENTS

TABLE B-1. EXPERIMENTAL CONDITIONS AND MAXIMUM OZONE PREDICTIONS

Date	Chamber	Isoprene (ppm of C)	NO_x (ppm)	Initial HONO (ppb)	HC/NO_x (ppmC/ ppm)	Temp Range (K)	Sky Conditions	Exptl O_3 Maximum (ppm)	Predicted O_3 Maximum (Explicit Isoprene Mechanism) (ppm)	Predicted/ Observed	Predicted O_3 Maximum (CBM-XR Isoprene Mechanism) (ppm)	Predicted/ Observed
(a) Isoprene Smog Chamber Runs												
6/20/80	Red	0.50	0.477	4	1.05	287-305	Cloudy	0.09	0.17	1.89	.07	.78
6/17/80	Red	0.50	0.192	4	2.60	291-303	Cloudy	0.35	0.43	1.23	.28	.8
6/23/80	Blue	1.27	0.211	4	6.02	286-306	Cloudy	0.57	0.66	1.16	.73	1.28
6/22/80	Blue	1.56	0.205	2	7.64	284-306	Clear	0.5[a] 0.55[b]	0.57[a] 0.67[b]	1.14 1.22	.73[d]	1.32
7/14/80	Blue	2.17	0.243	6	8.93	292-307	Clear	0.5[a] 0.63[b]	0.58[a] 0.69[b]	1.16 1.10	.75[d]	1.19
7/16/80	Blue	1.97	0.188	6	10.48	293-310	Clear	0.55[c] 0.83[b]	0.49[c] 0.63[b]	0.89 0.76	.6[a] .70[b]	1.09 .84
6/17/80	Blue	1.40	0.098	2	14.29	291-303	Cloudy	0.39[c] 0.41[b]	0.33[c] 0.39[b]	1.14 0.95	.42[c] .42[b]	1.08 1.02
6/22/8	Red	3.83	0.203	2	18.89	284-306	Clear	0.34[c] 0.39[b]	0.46[c] 0.46[b]	1.35 1.18	.33[c] .39[b]	0.97 1.00
7/14/80	Red	4.95	0.253	6	19.57	292-307	Clear	0.39[c] 0.43[b]	0.42[c] 0.43[b]	1.08 1.00	.48[d]	1.12
7/16/80	Red	4.01	0.186	10	21.56	293-310	Clear	0.37[c] 0.65[b]	0.34[c] 0.38[b]	0.92 0.58	.37[d]	0.57

TABLE B-1 (concluded)

(b) Methacrolein and Methyl Vinyl Ketone Smog Chamber Runs

Date	Chamber	Metha-crolein (ppm)	NO_x (ppm)	Initial HONO (ppb)	HC/NO_x (ppmC/ppm)	Temp Range (K)	Sky Conditions	Exptl O_3 Maximum (ppm)	Predicted O_3 Maximum (Explicit Isoprene Mechanism) (ppm)	Predicted/ Observed	Predicted O_3 Maximum (CBM-XR Isoprene Mechanism)	Predicted/ Observed
8/05/81	Red	0.4	0.44	5		296-306	Clear	0.8			.9	1.13
8/13/81	Blue	0.475	0.47	5		294-302	Clear	0.8			.8	1.0

Date	Chamber	Methyl Vinyl Ketone (ppm)	NO_x (ppm)	Initial HONO (ppb)	HC/NO_x (ppmC/ppm)	Temp Range (K)	Sky Conditions	Exptl O_3 Maximum (ppm)	Predicted O_3 Maximum (Explicit Isoprene Mechanism) (ppm)	Predicted/ Observed	Predicted O_3 Maximum (CBM-XR Isoprene Mechanism)	Predicted/ Observed
8/05/81	Blue	0.378	0.445	5		296-306	Clear	0.8			.72	0.9
8/13/81	Red	0.497	0.46	5		294-302	Clear	0.82			.78	0.95

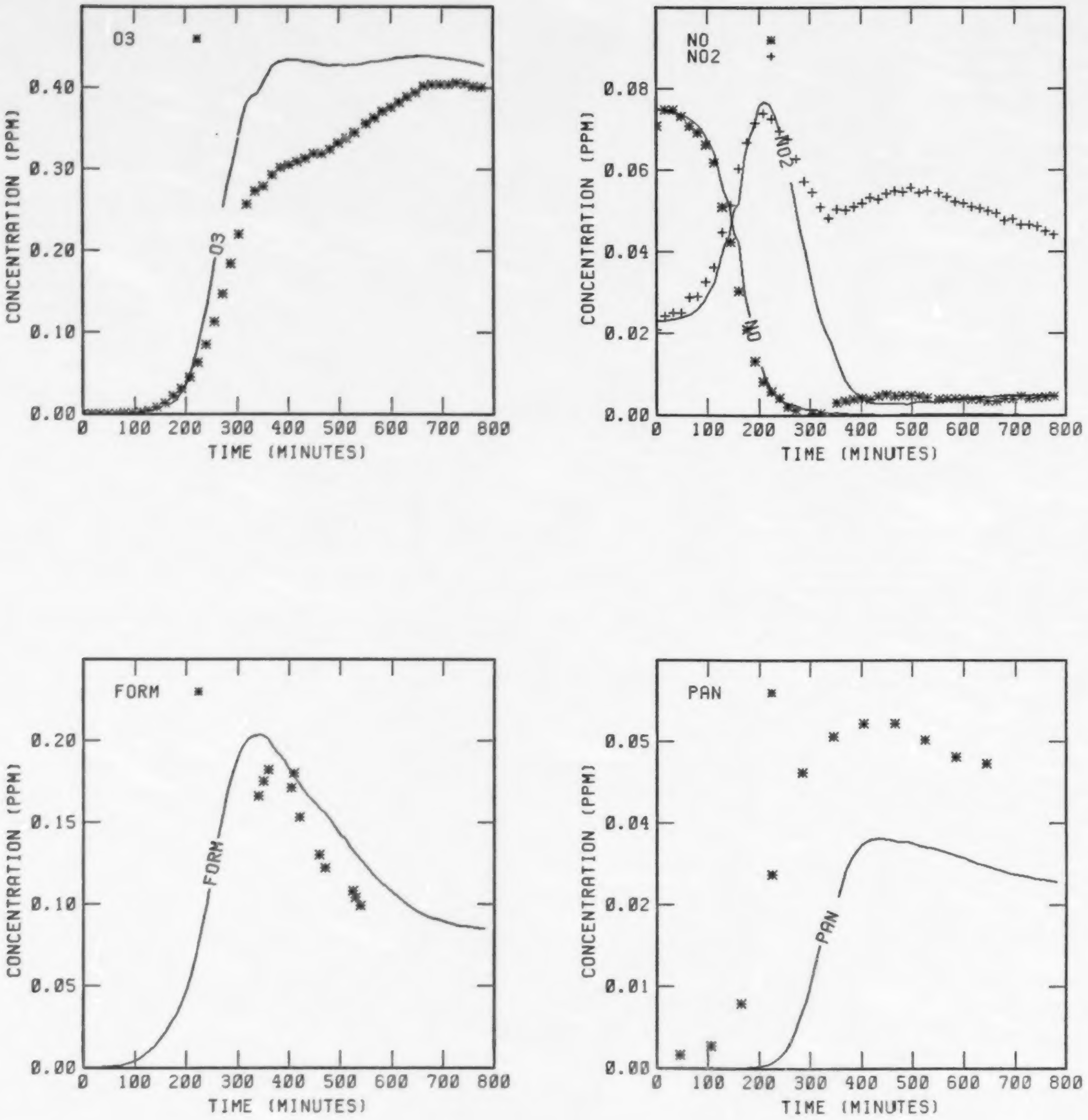

FIGURE B-1. SIMULATION RESULTS FOR
UNCB 61780

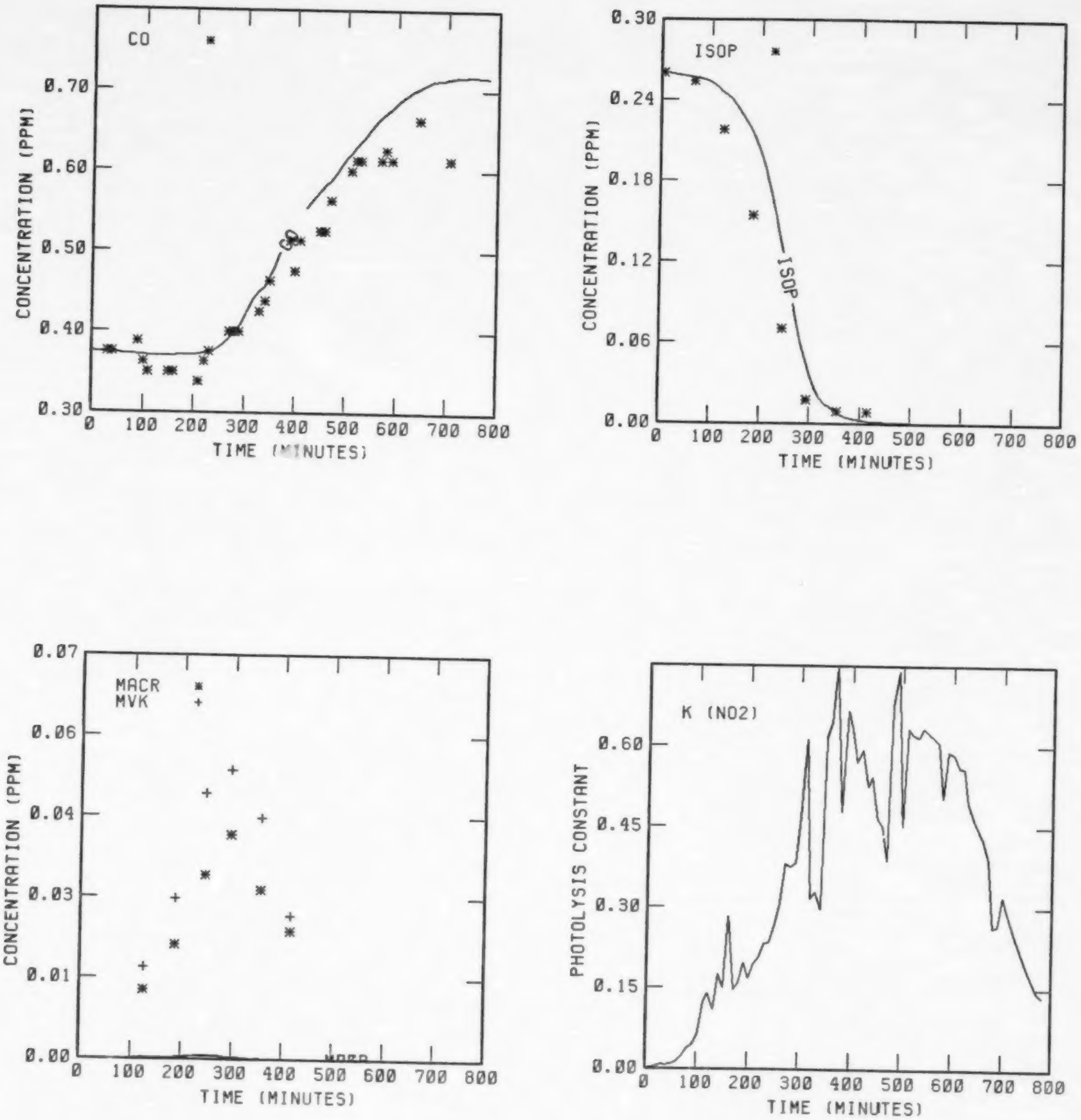

FIGURE B-1. SIMULATION RESULTS FOR
UNCB 61780

(continued)

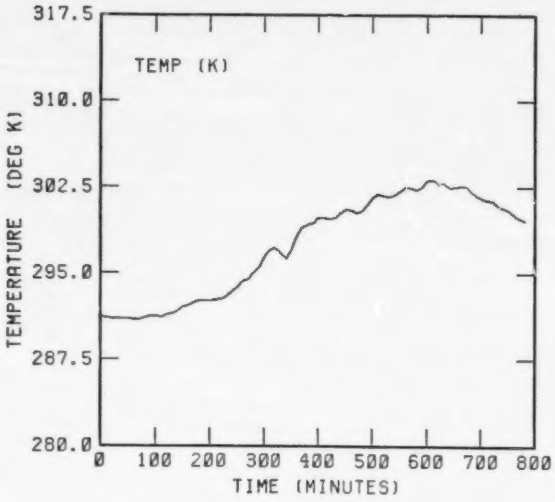

FIGURE B-1. SIMULATION RESULTS FOR UNCB 61780

(concluded)

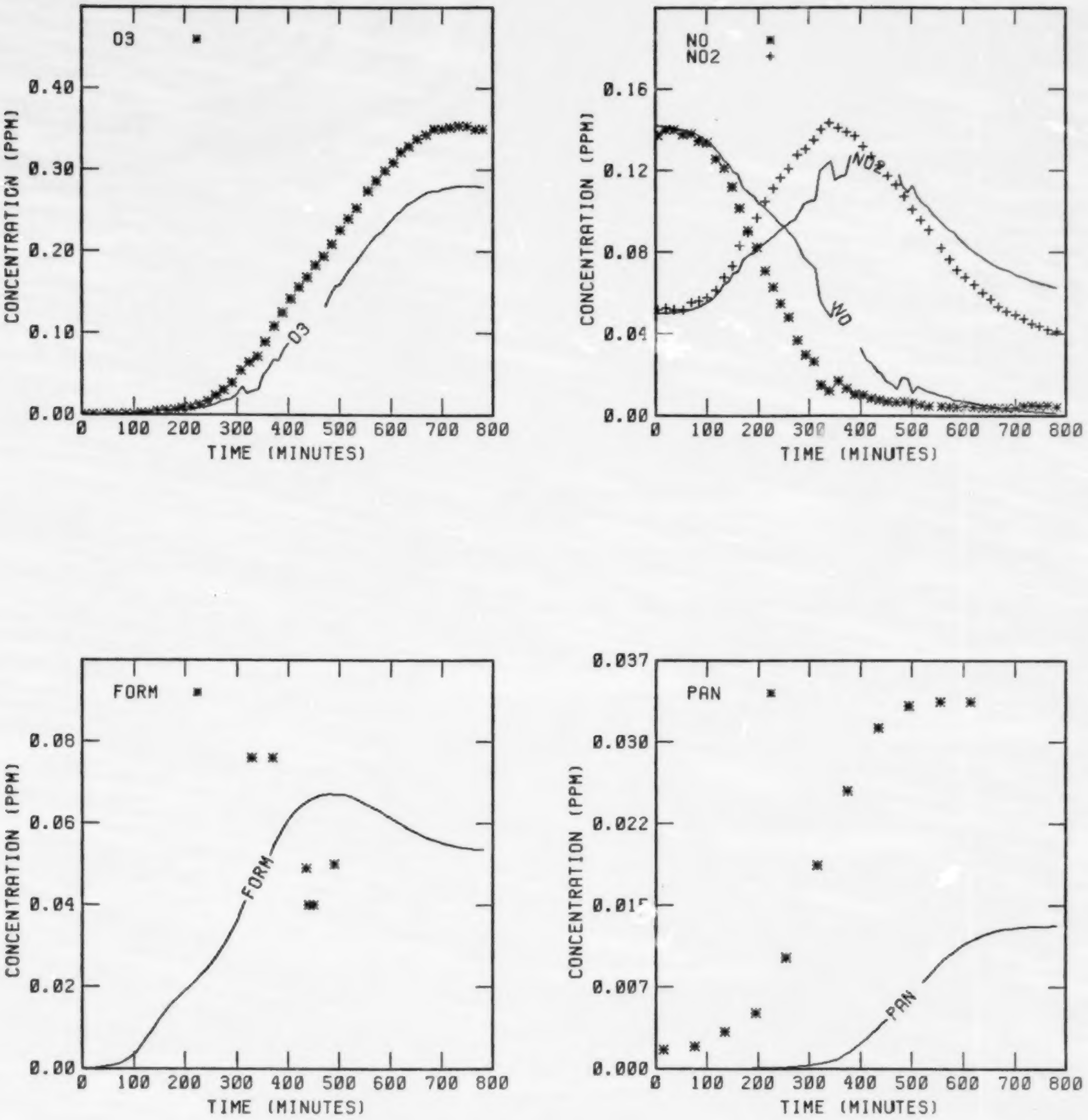

FIGURE B-2. SIMULATION RESULTS FOR
UNCR 61780

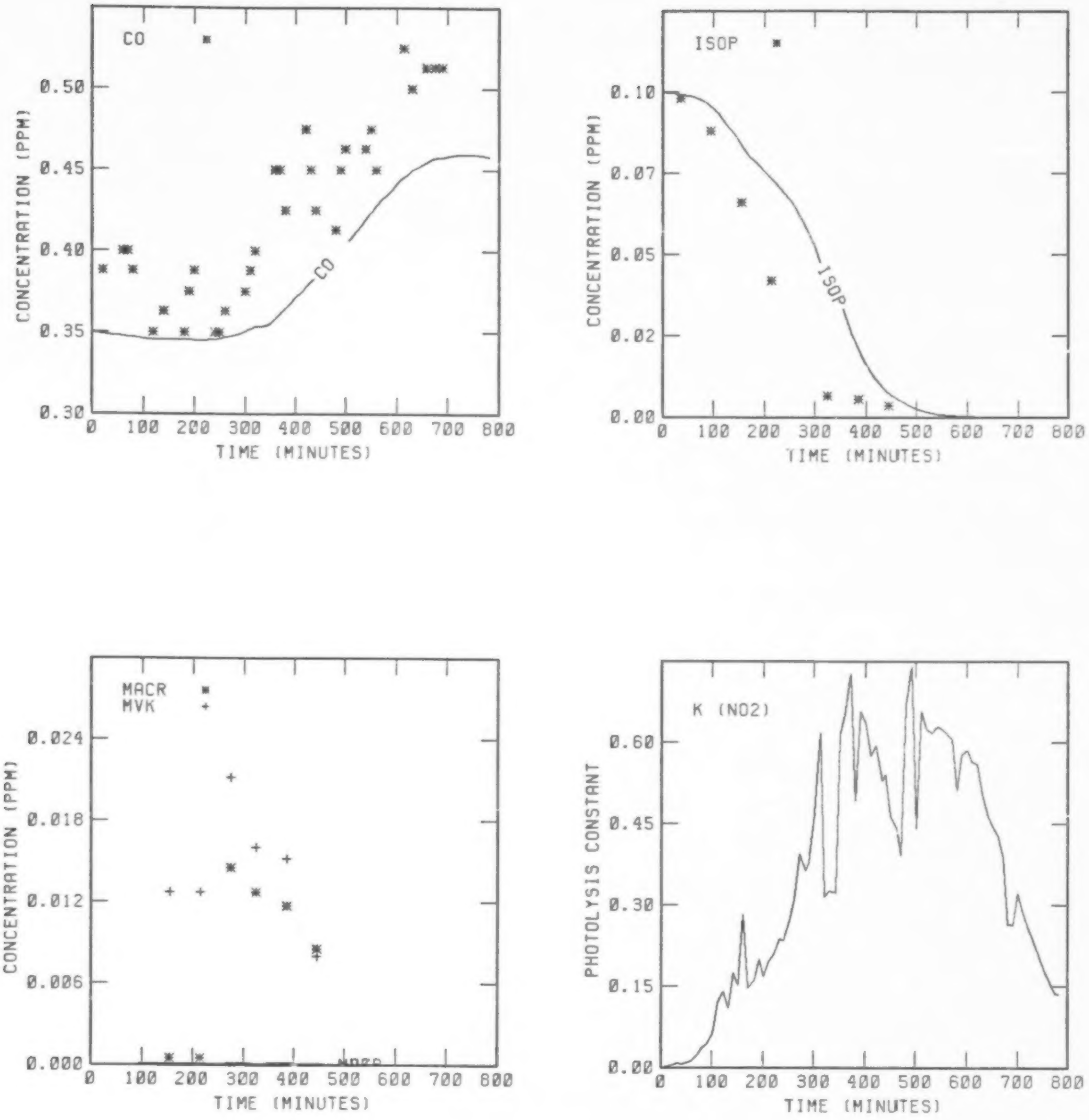

FIGURE B-2. SIMULATION RESULTS FOR
UNCR 61780

(continued).

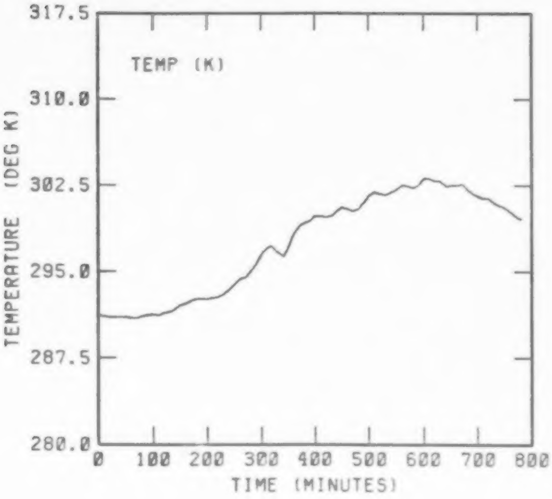

FIGURE B-2. SIMULATION RESULTS FOR UNCR 61780

(concluded)

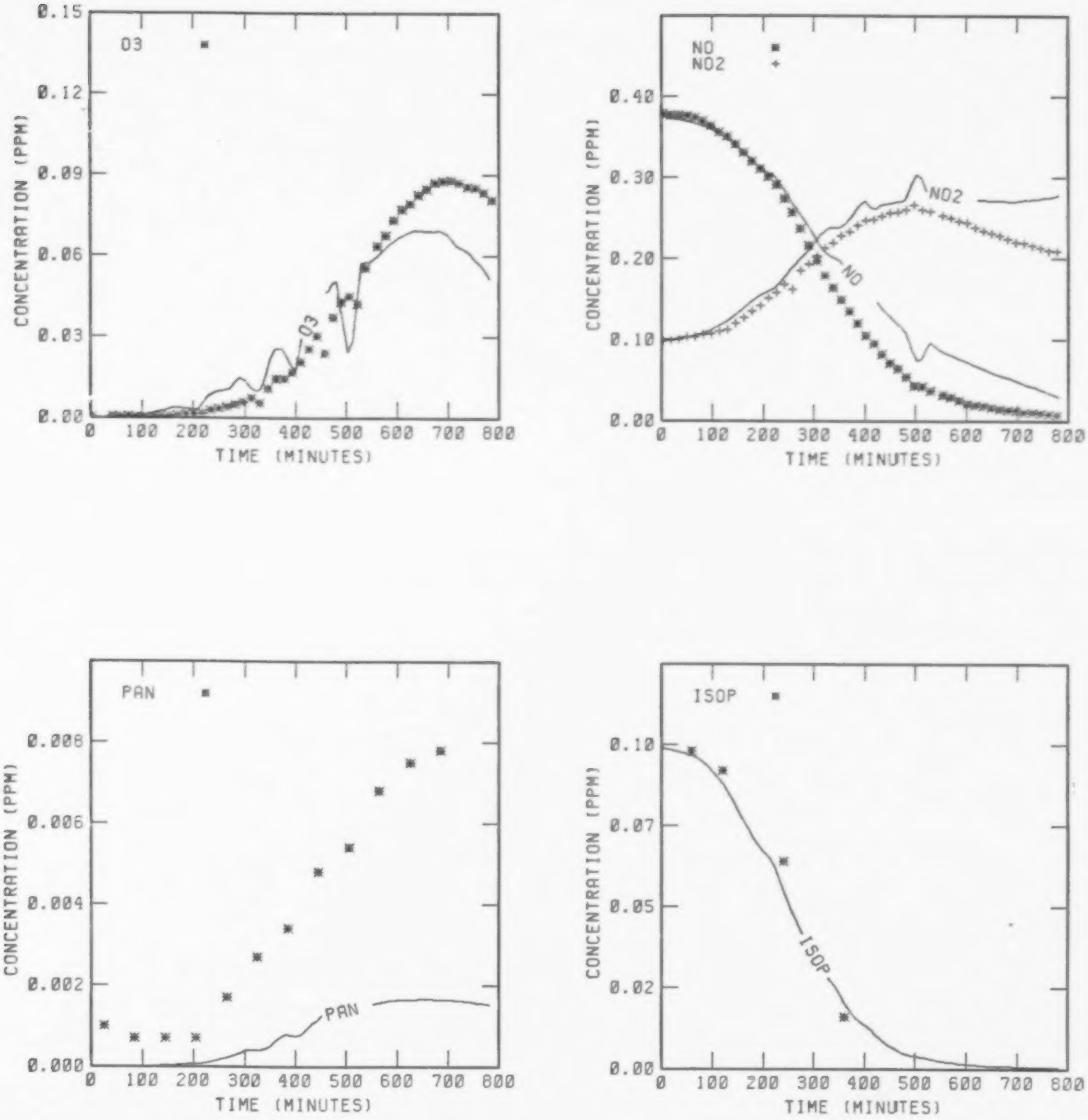

FIGURE B-3 . SIMULATION RESULTS FOR
UNCR 62080

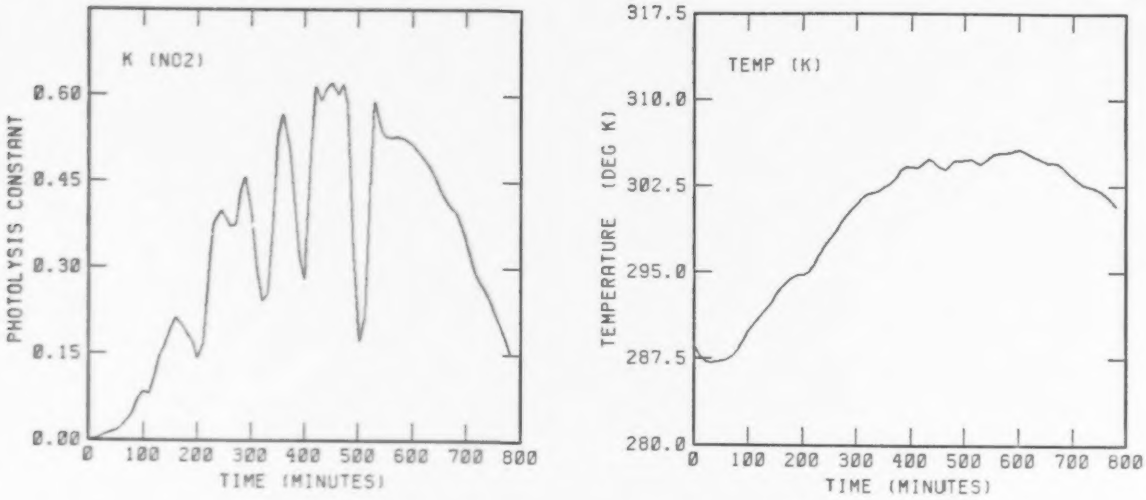

FIGURE B-3. SIMULATION RESULTS FOR
UNCR 62080

(concluded)

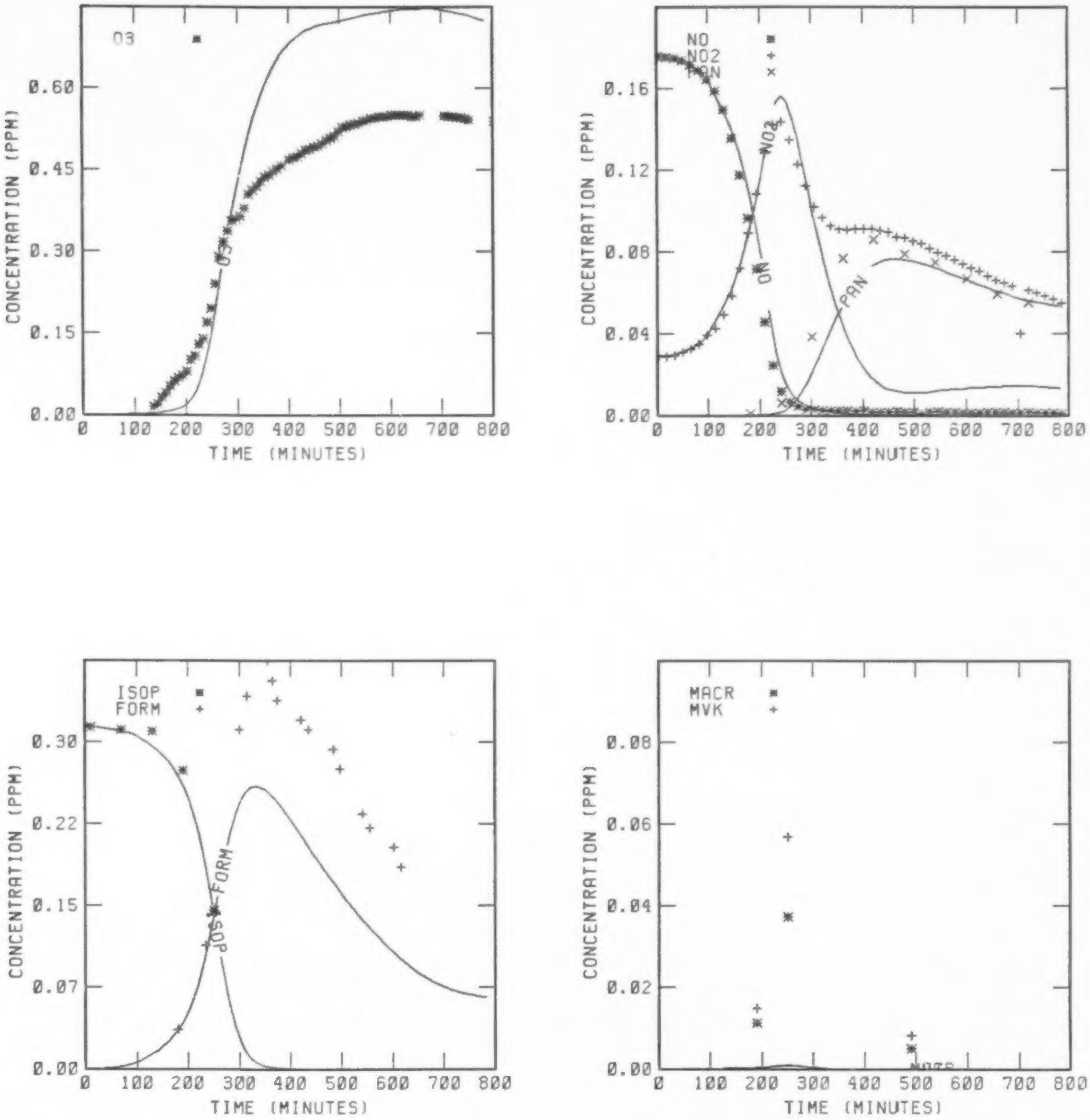

FIGURE **B-4.** SIMULATION RESULTS FOR
UNCB 62280

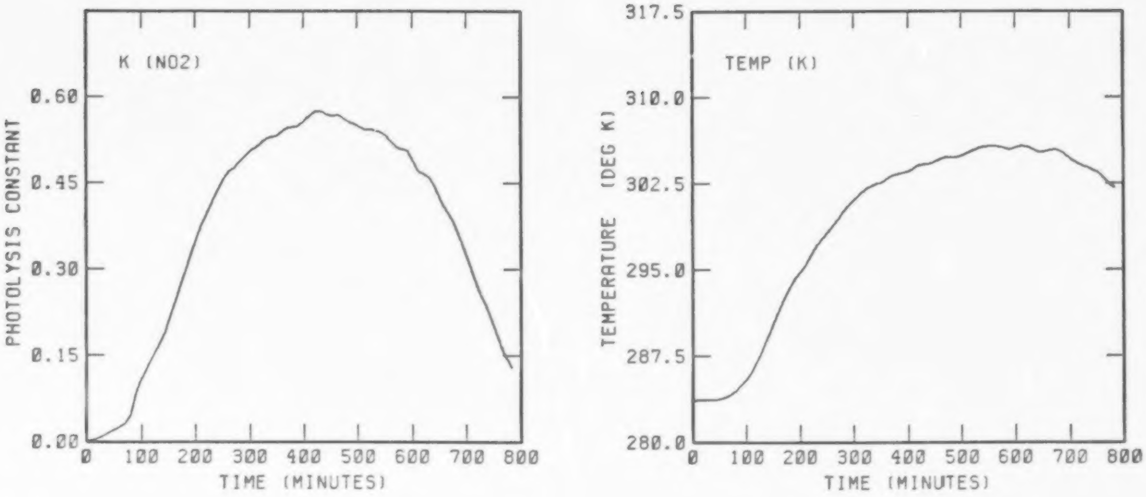

FIGURE B-4. SIMULATION RESULTS FOR UNCB 62280

(concluded)

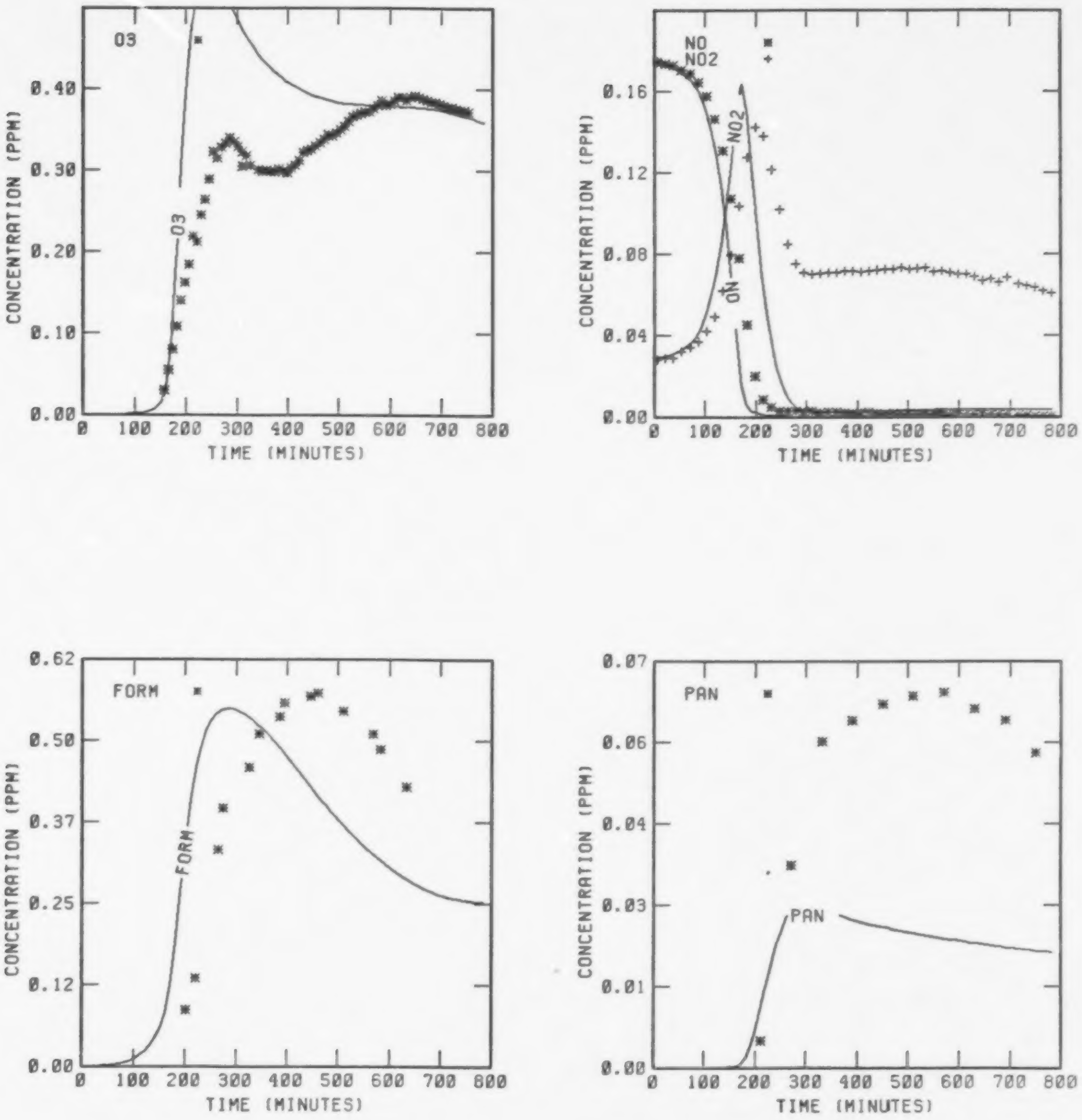

FIGURE B-5. SIMULATION RESULTS FOR
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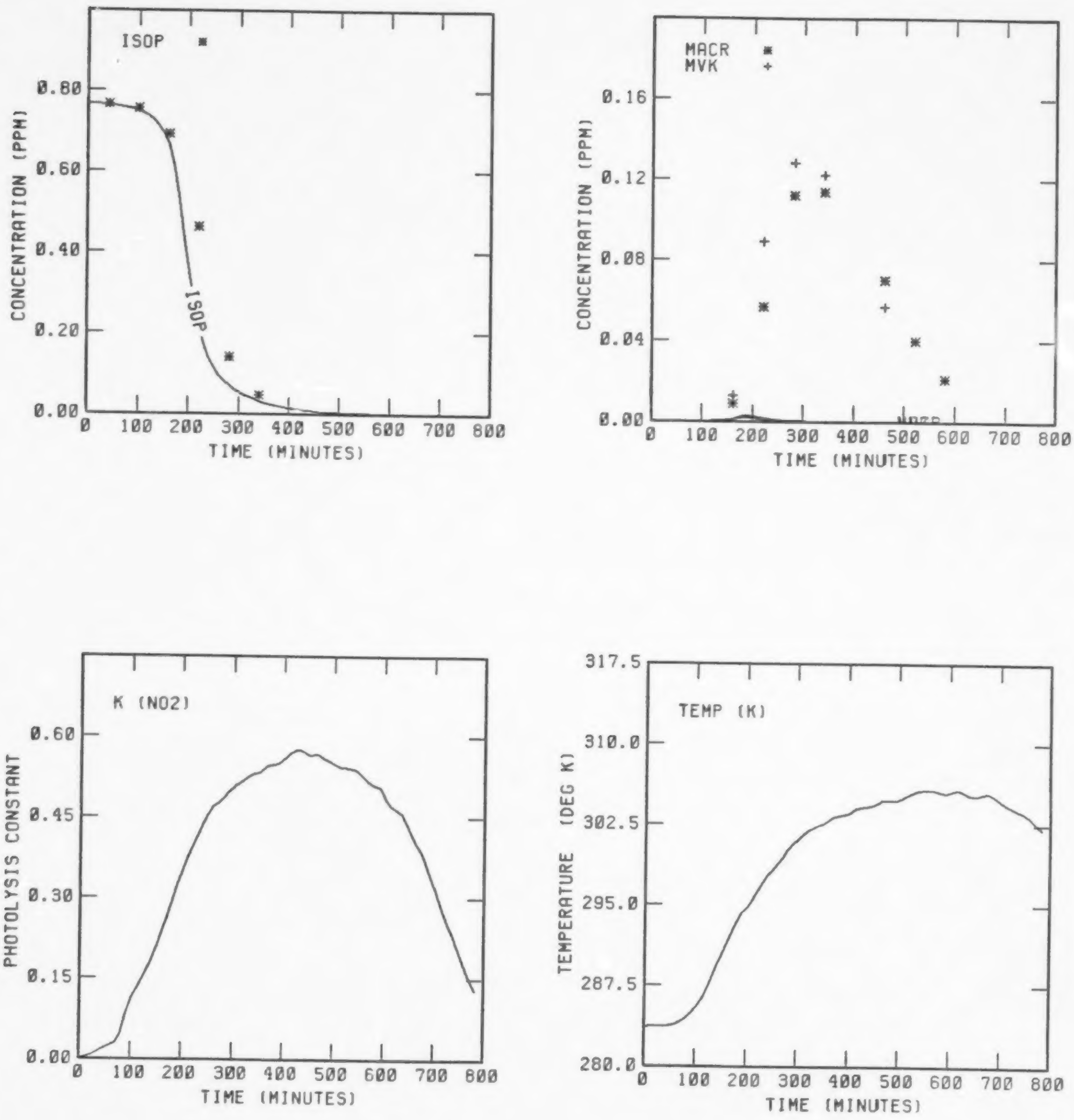

FIGURE B-5. SIMULATION RESULTS FOR
UNCR 62280

(concluded)

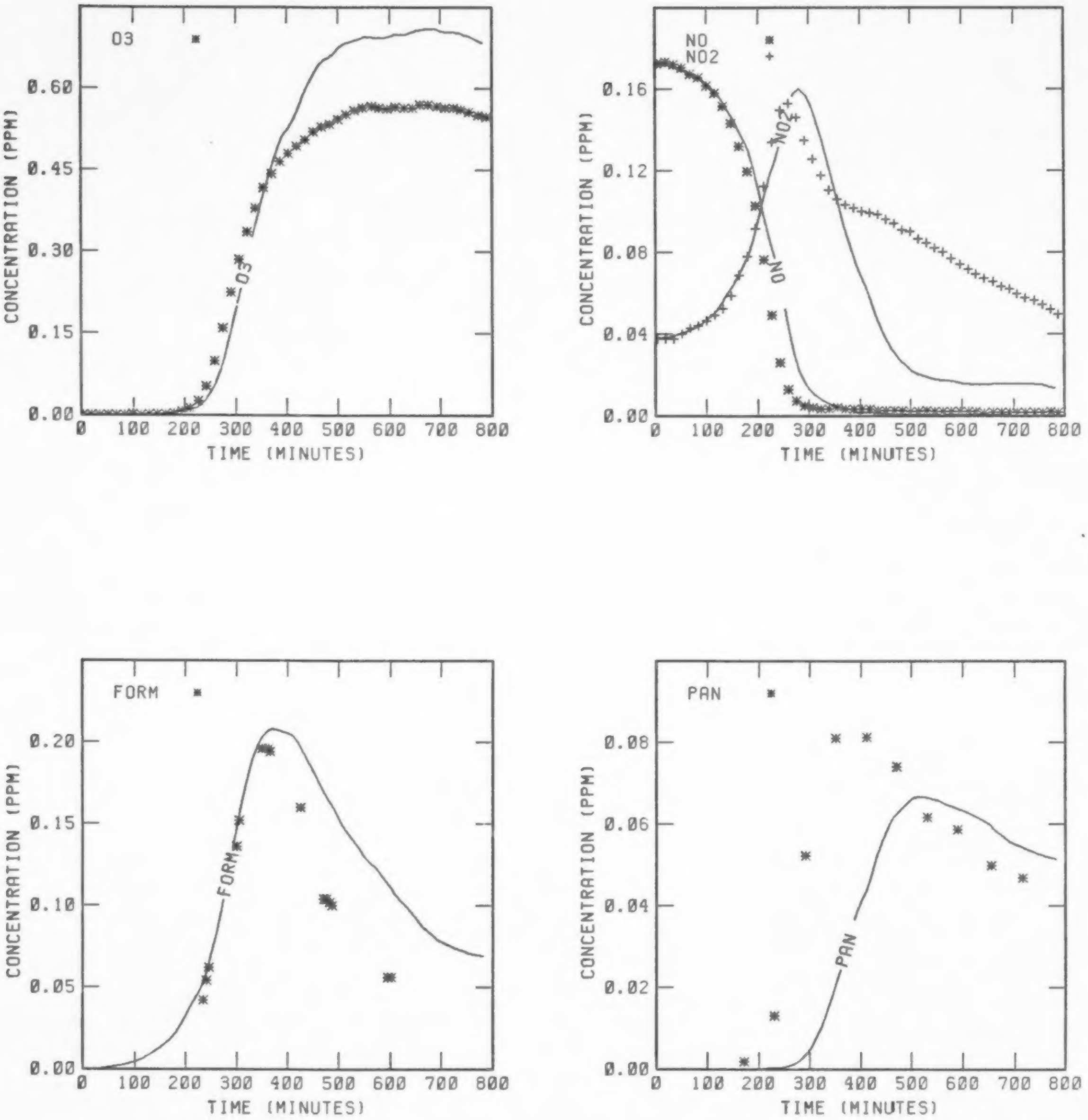

FIGURE B-6. SIMULATION RESULTS FOR
UNCB 62380

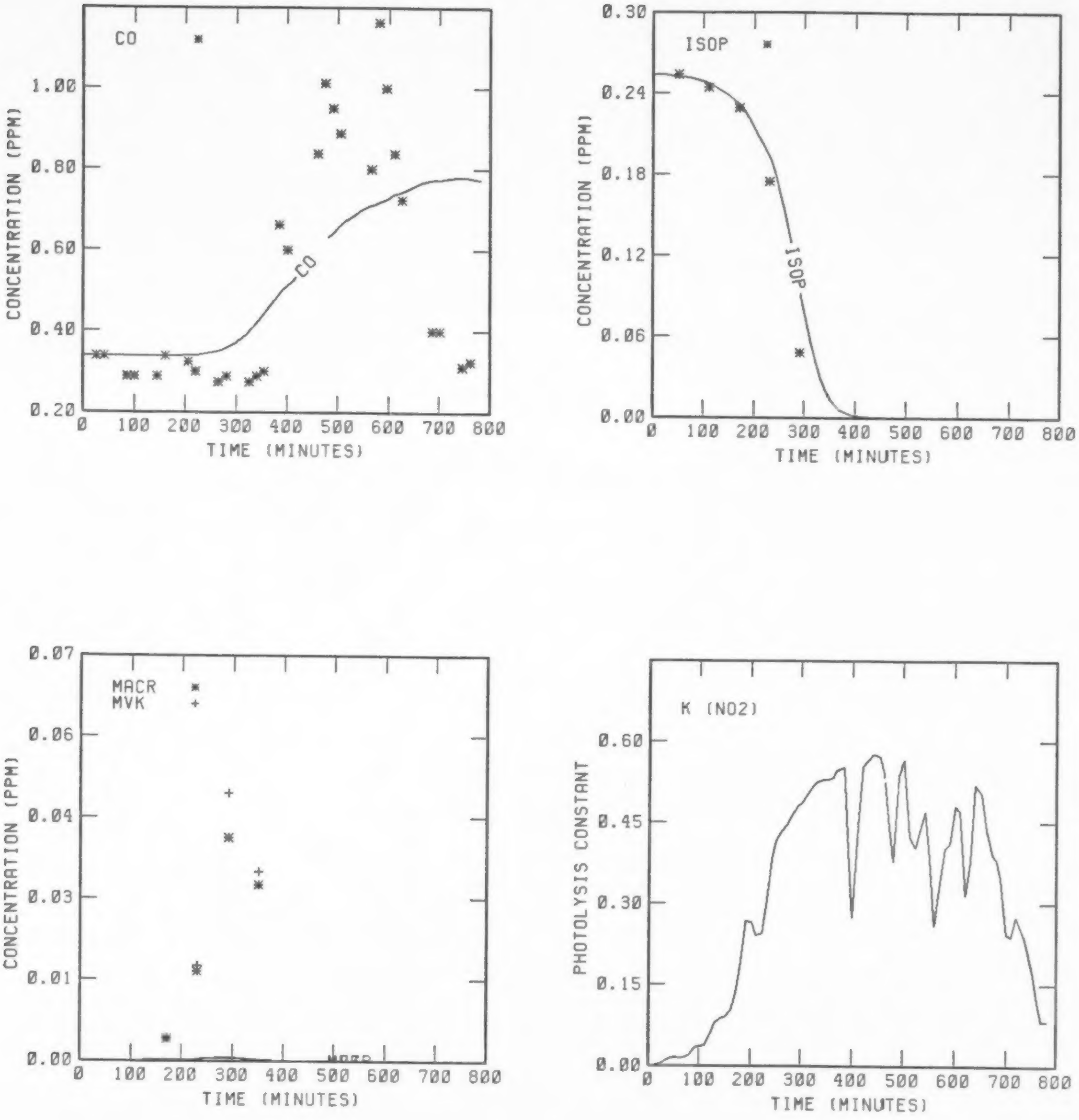

FIGURE B-6. SIMULATION RESULTS FOR
UNCB 62380

(continued)

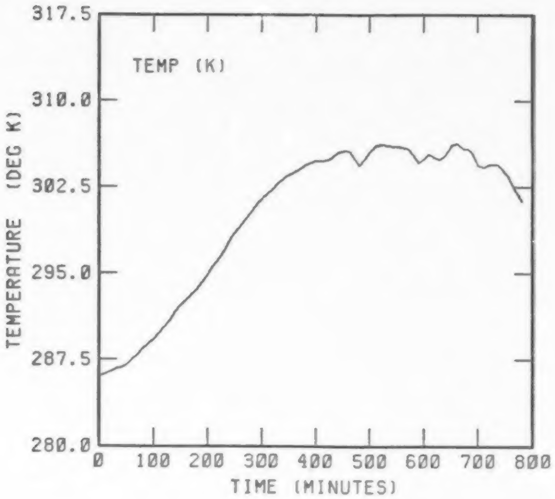

FIGURE B-6. SIMULATION RESULTS FOR
UNCB 62380

(concluded).

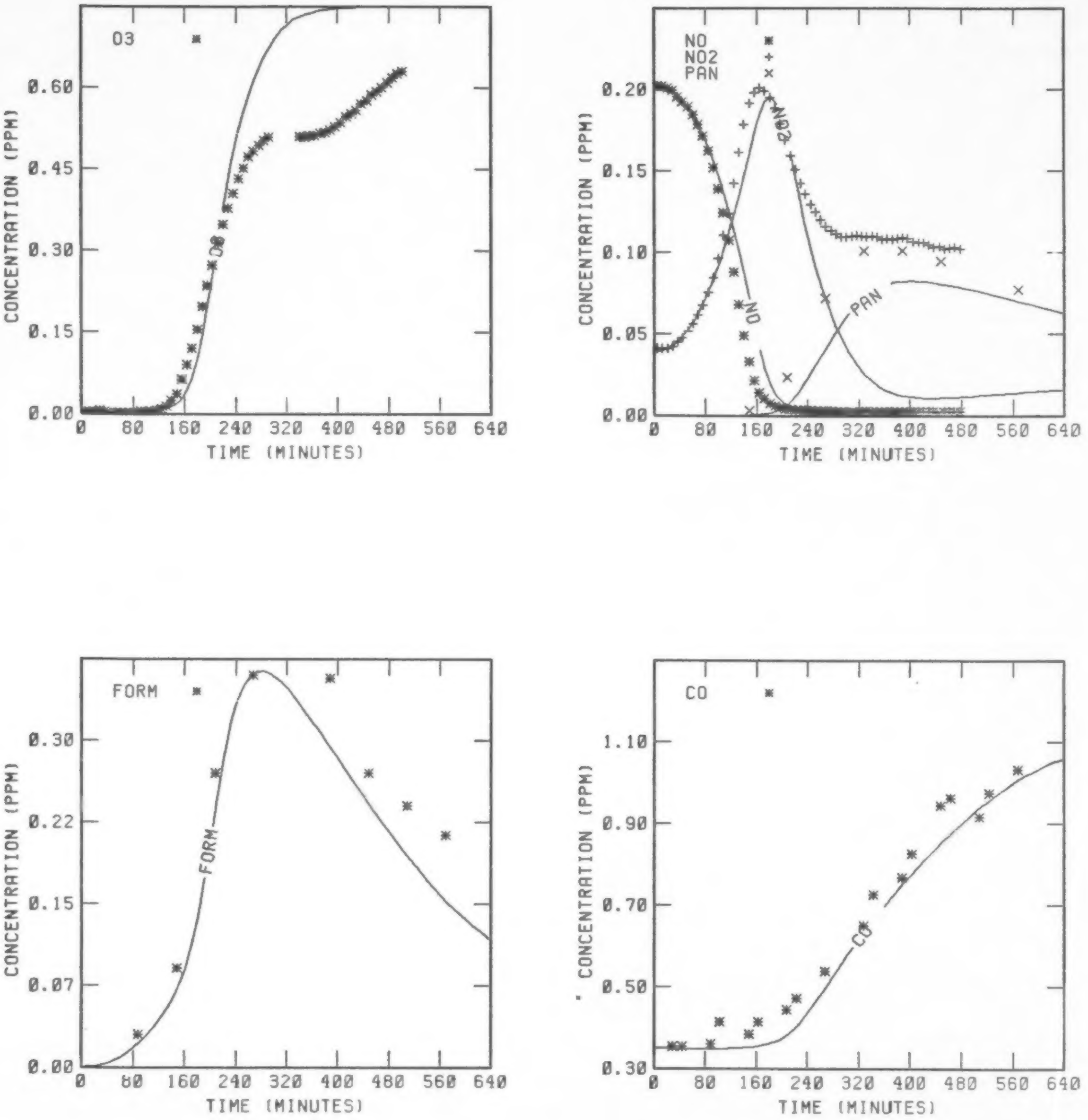

FIGURE B-7. SIMULATION RESULTS FOR
UNCB 71480

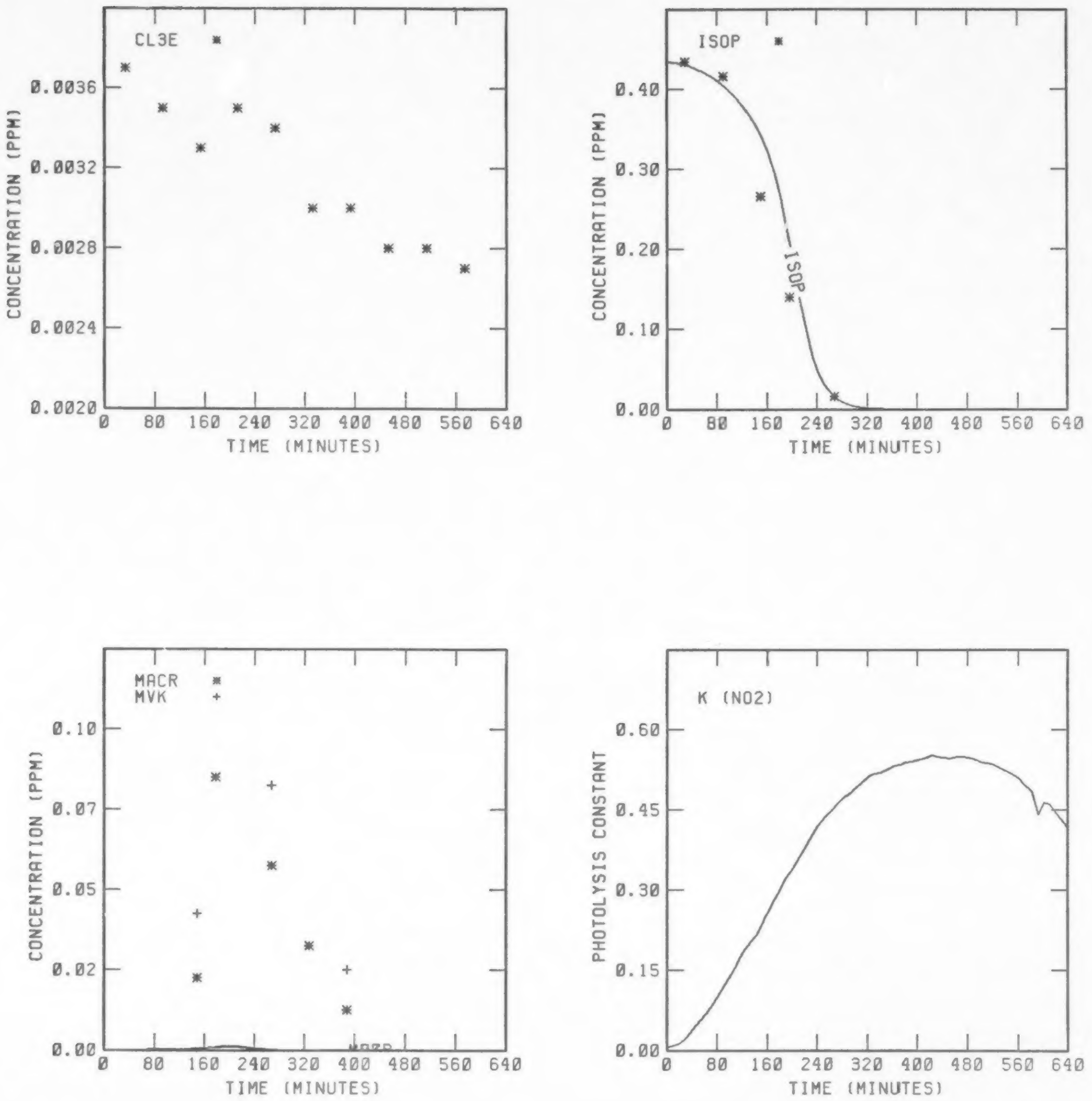

FIGURE B-7 . SIMULATION RESULTS FOR
UNCB 71480

(continued)

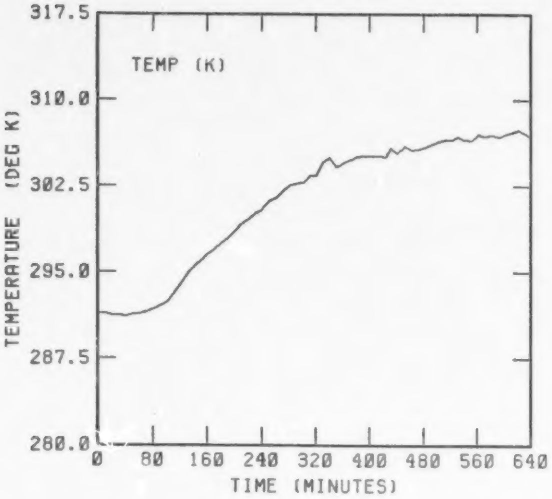

FIGURE B-7. SIMULATION RESULTS FOR
UNCB 71480

(concluded)

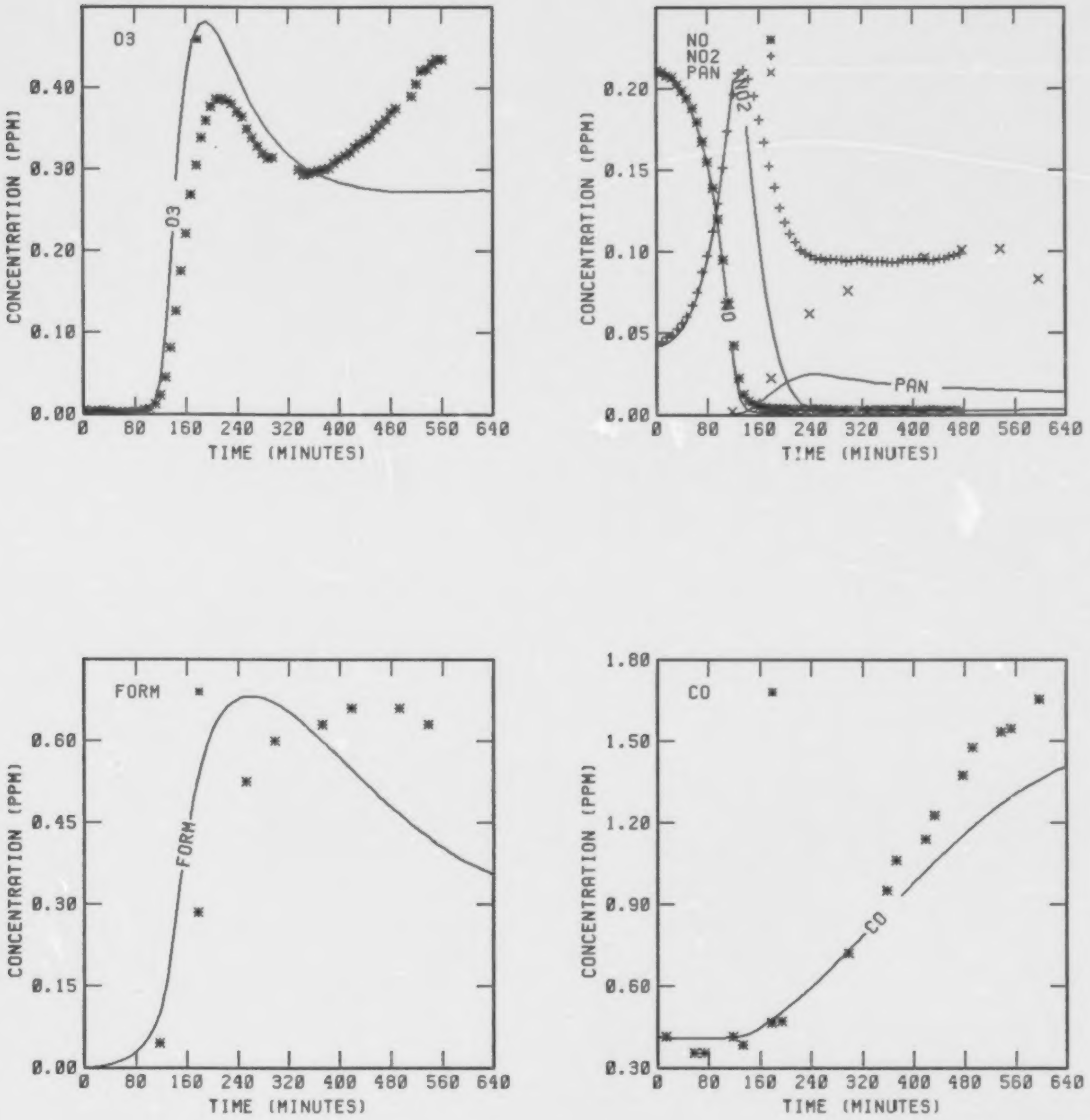

FIGURE B-8. SIMULATION RESULTS FOR
UNCR 71480

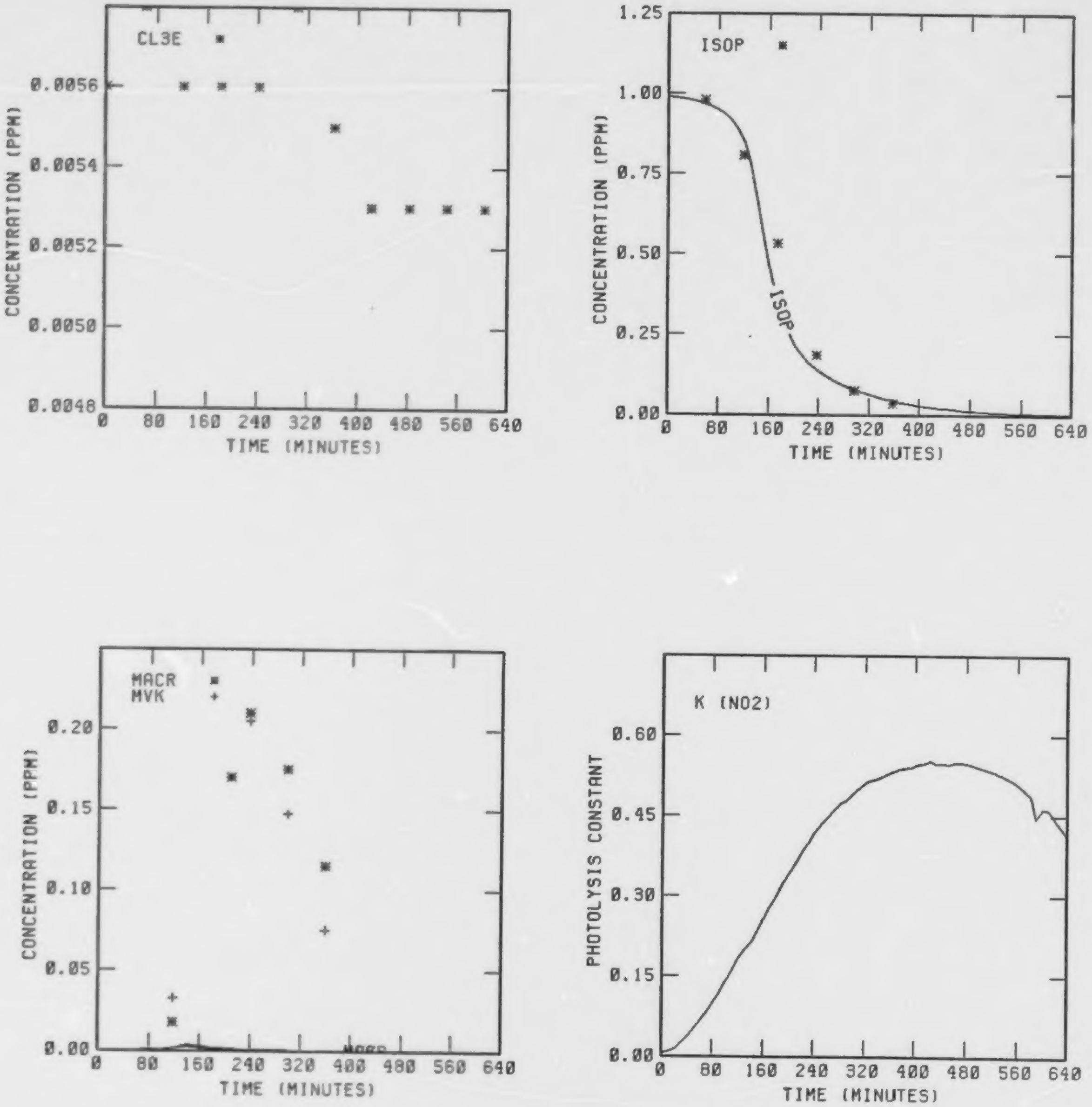

FIGURE B-8. SIMULATION RESULTS FOR
UNCR 71480

(continued)

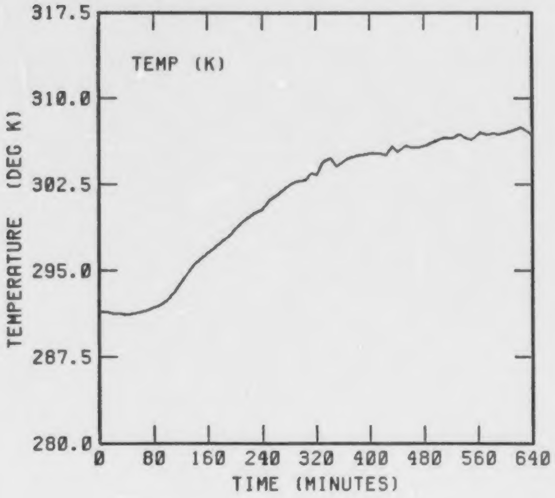

FIGURE B-8 . SIMULATION RESULTS FOR
UNCR 71480

(concluded)

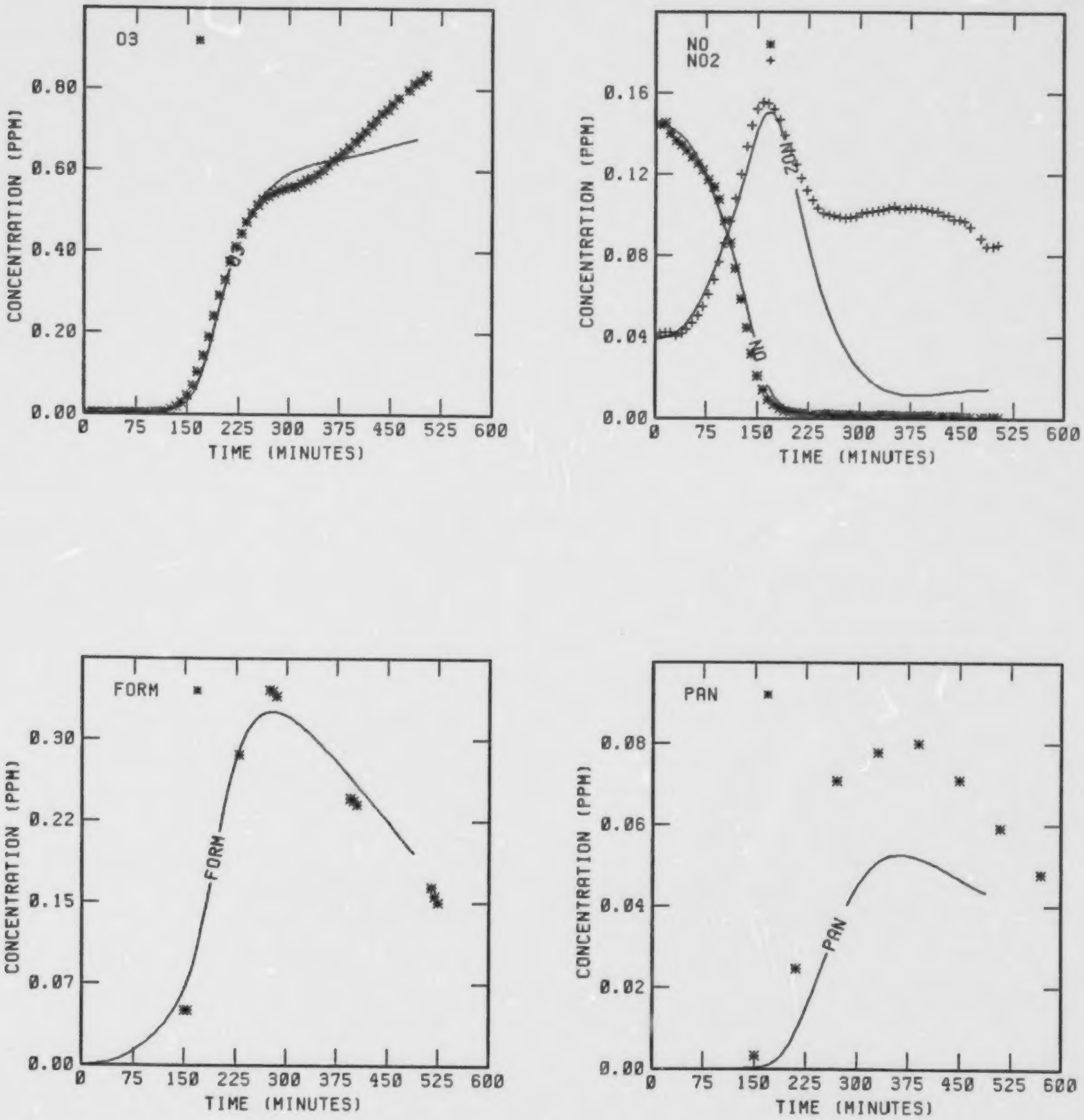

FIGURE B-9 .. SIMULATION RESULTS FOR
UNCB 71680

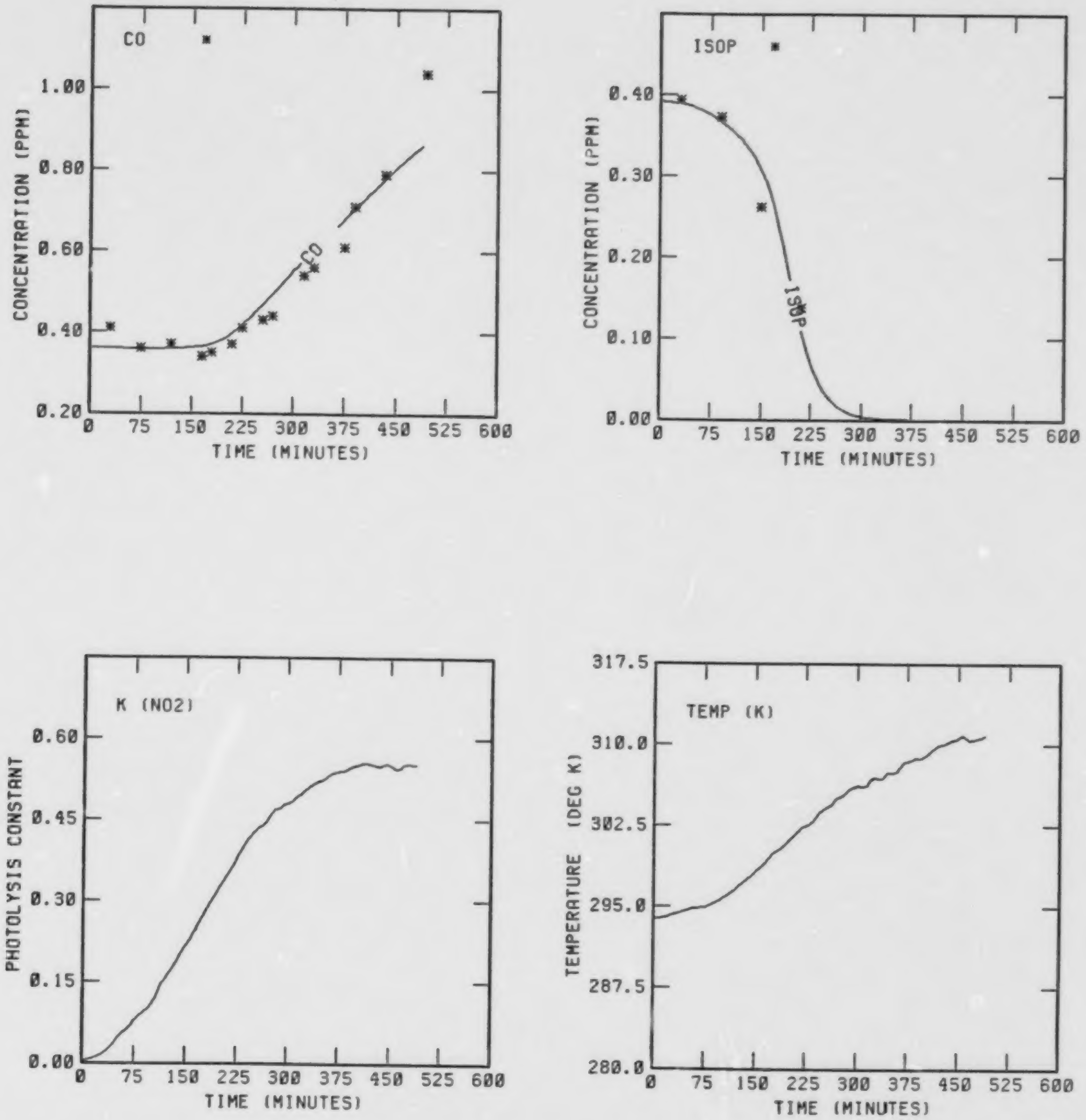

FIGURE B-9. SIMULATION RESULTS FOR
UNCB 71680
(concluded)

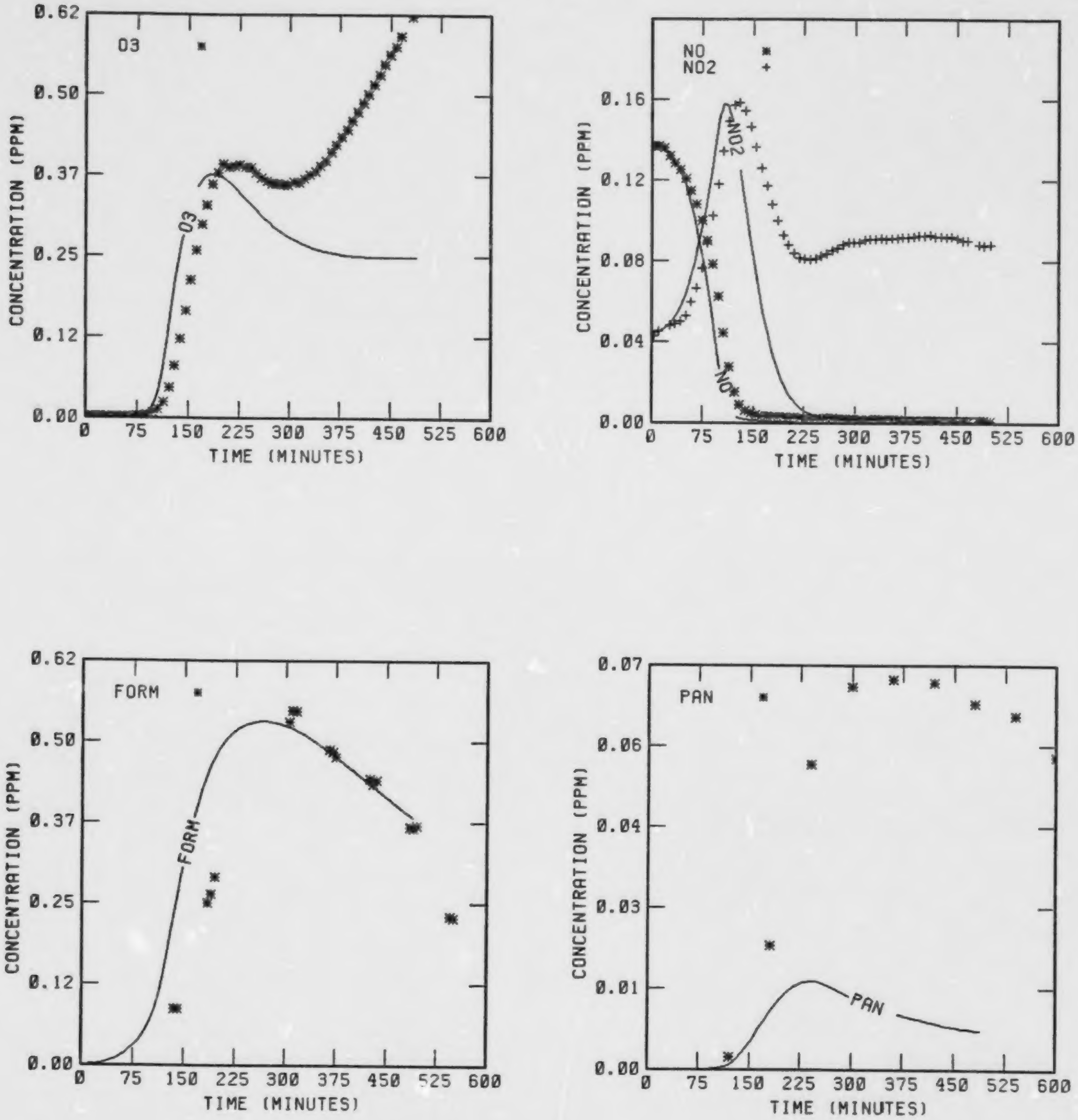

FIGURE B-10. SIMULATION RESULTS FOR
UNCR 71680

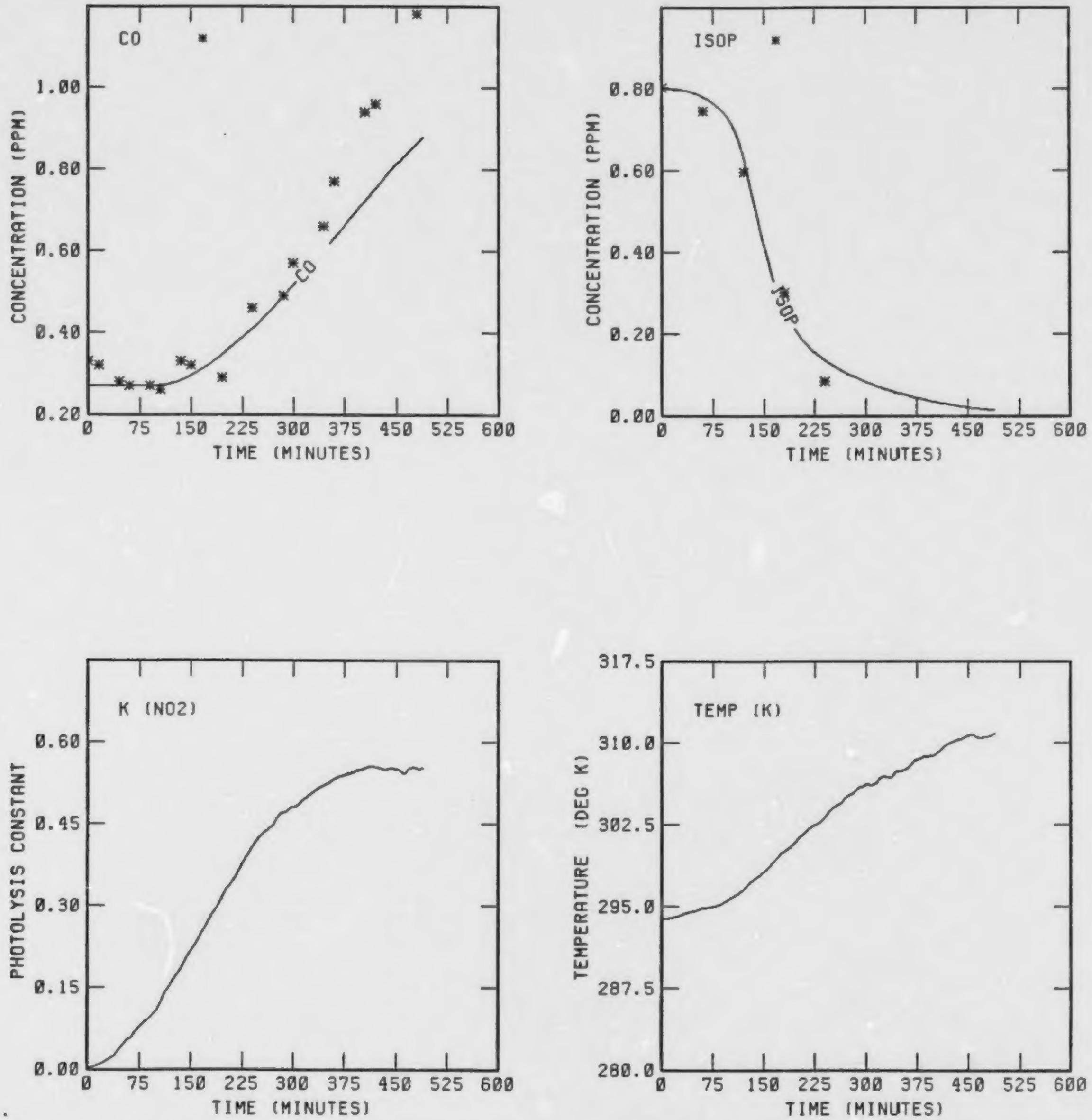

FIGURE B-10. SIMULATION RESULTS FOR
UNCR 71680
(concluded)

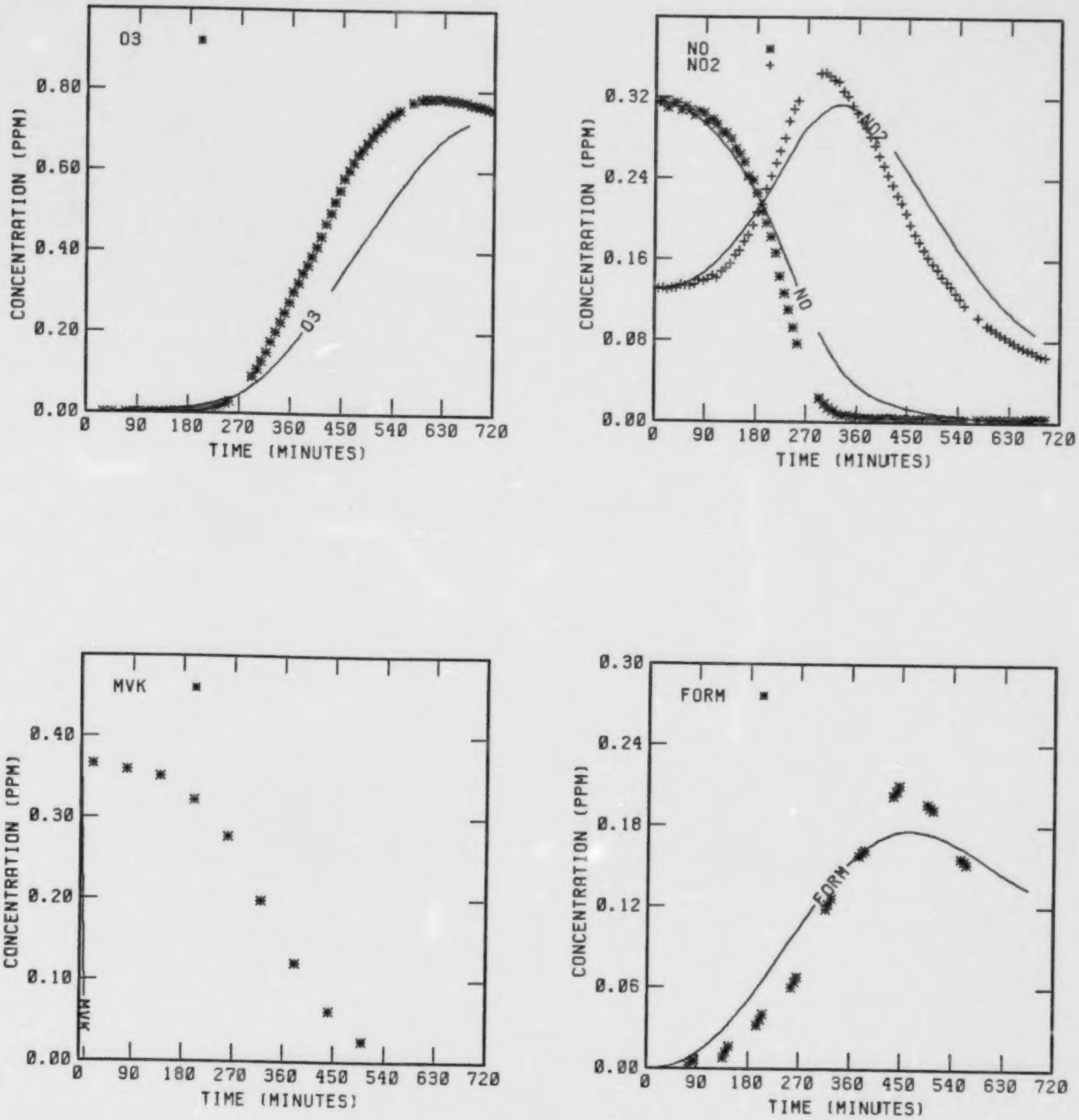

FIGURE B-11. SIMULATION RESULTS FOR
UNCB 80581

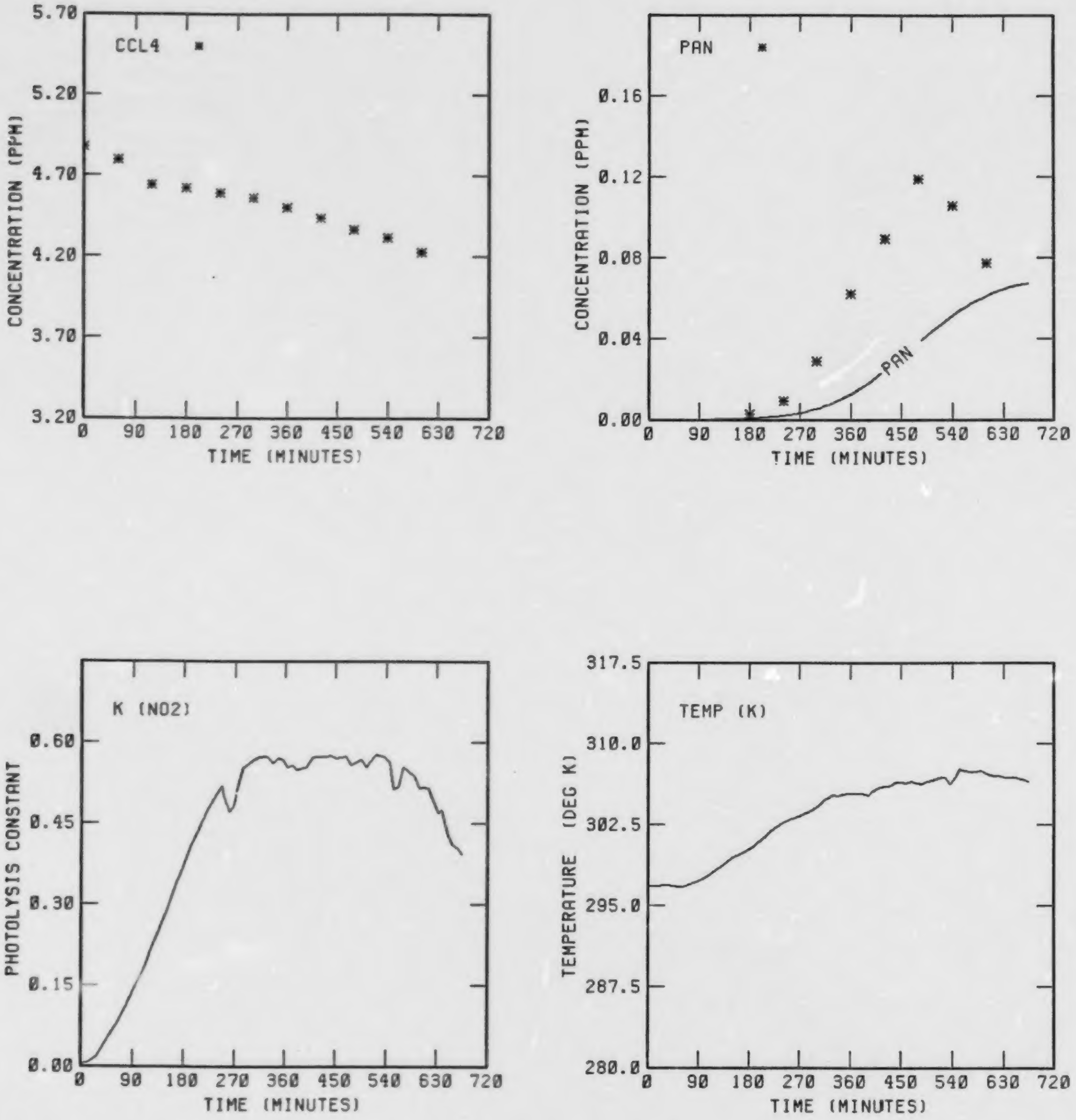

FIGURE B-11. SIMULATION RESULTS FOR
UNCB 80581
(concluded)

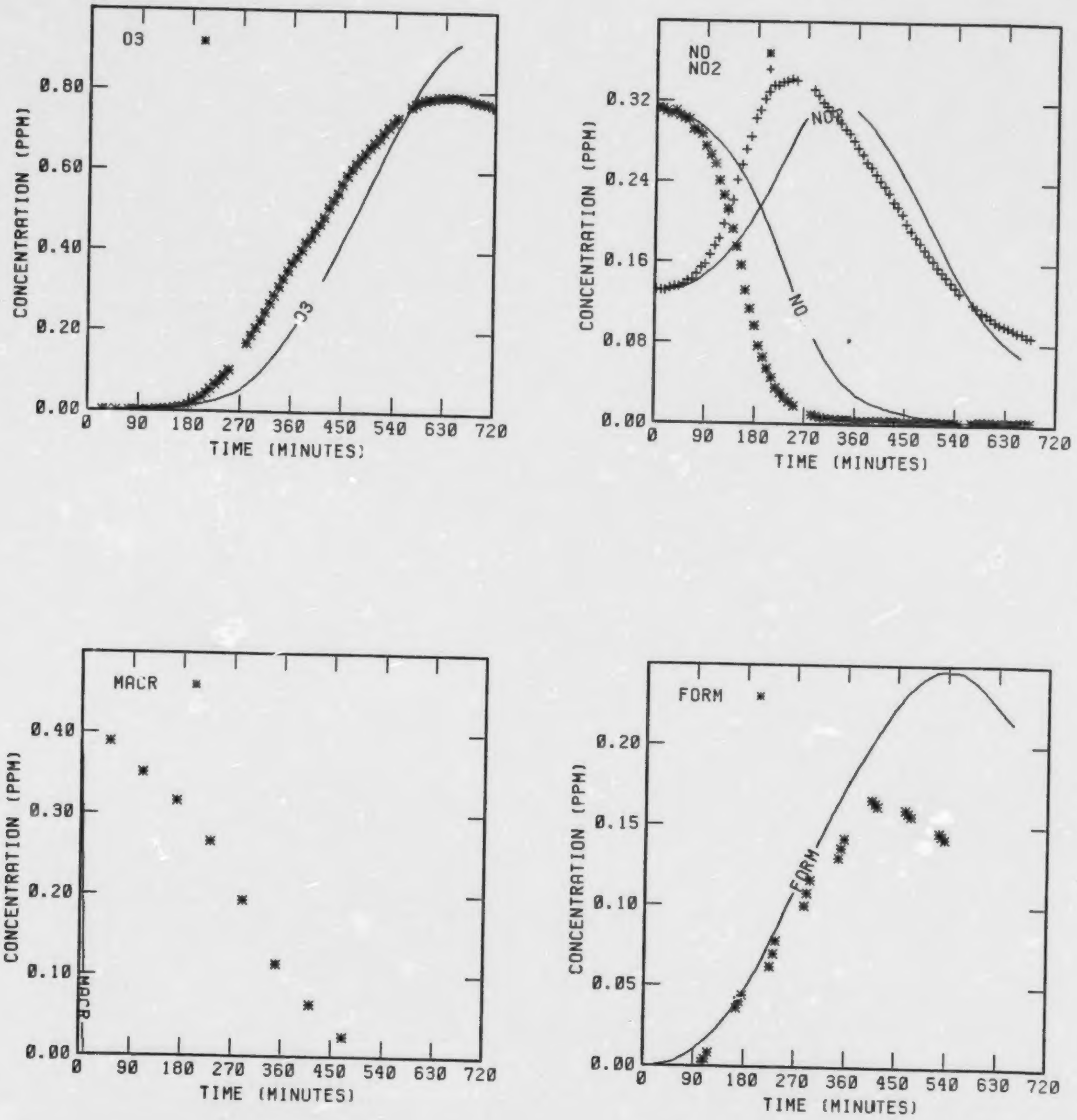

FIGURE B-12. SIMULATION RESULTS FOR
UNCR 80581

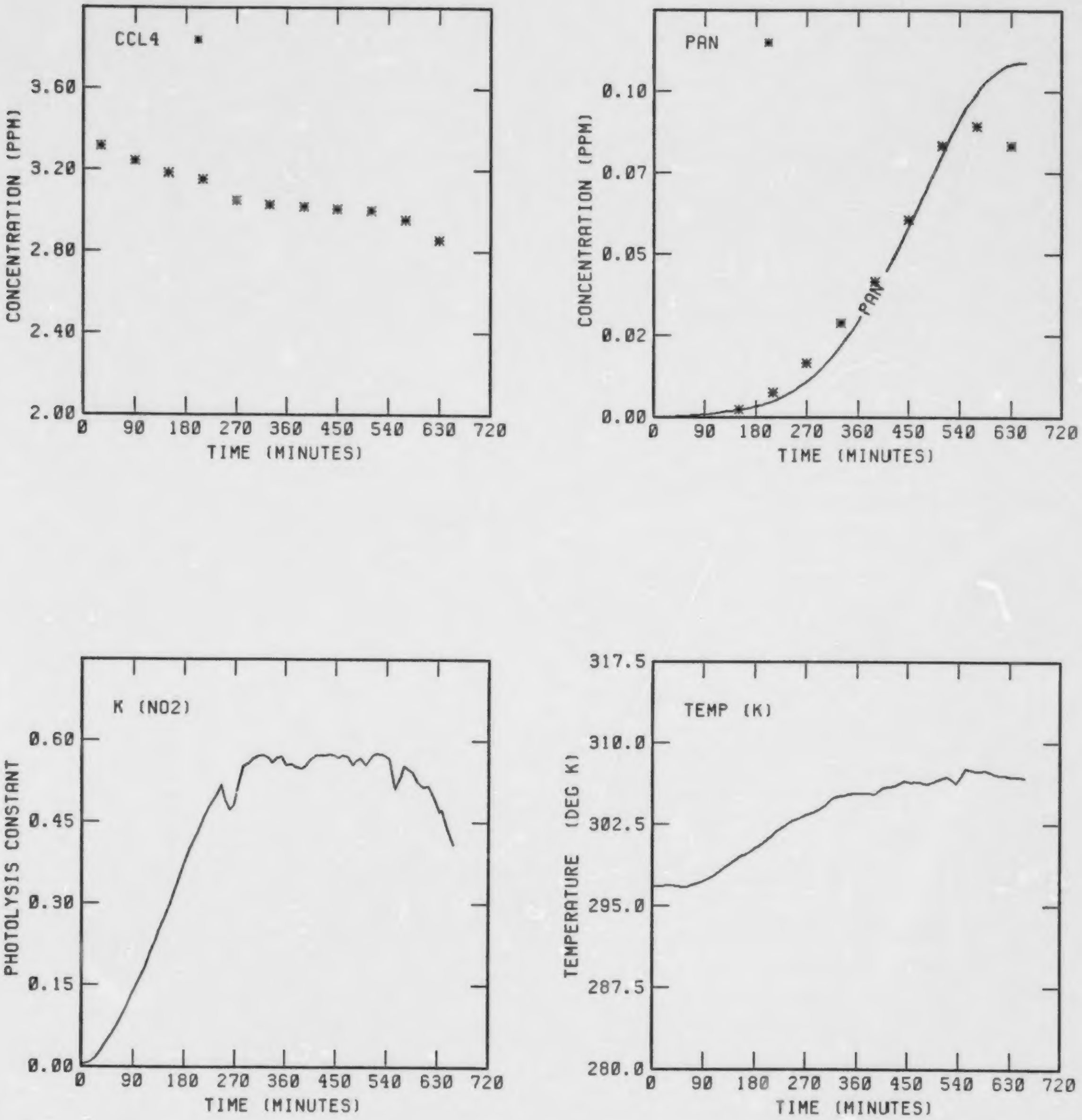

FIGURE B-12. SIMULATION RESULTS FOR
UNCR 80581

(concluded)

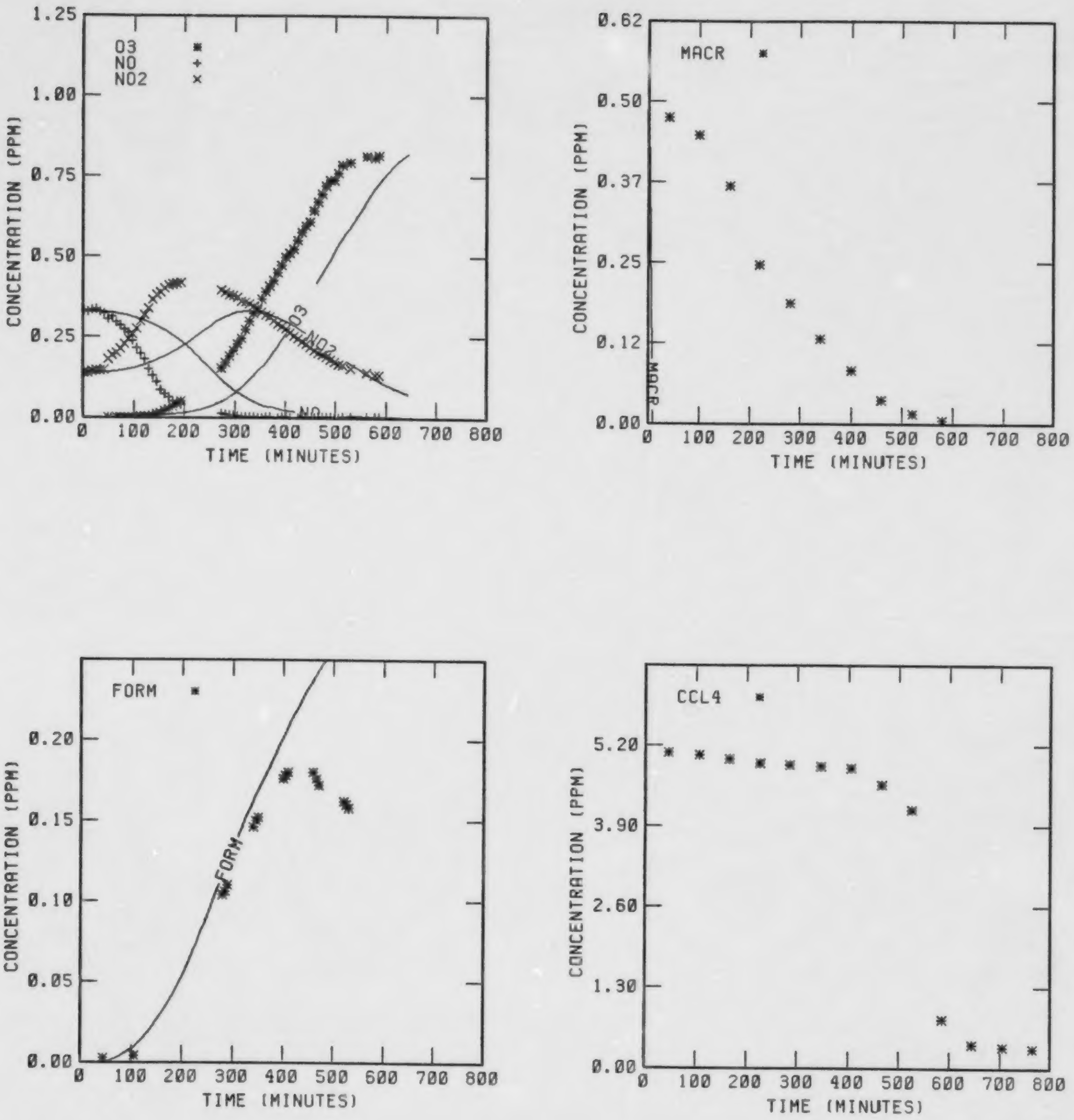

FIGURE B-13. SIMULATION RESULTS FOR
UNCB 81381

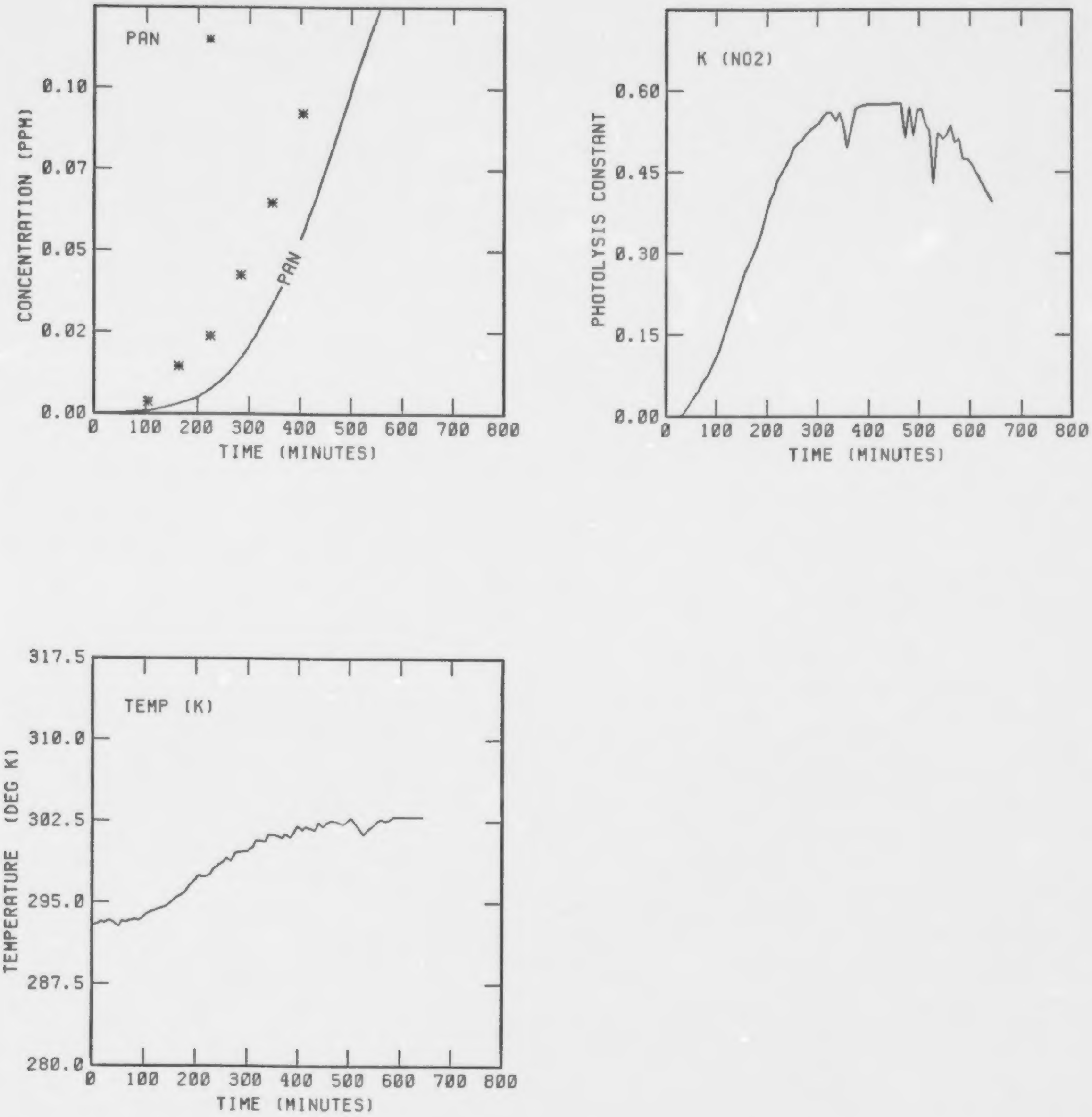

FIGURE **B-13**. SIMULATION RESULTS FOR
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(concluded)

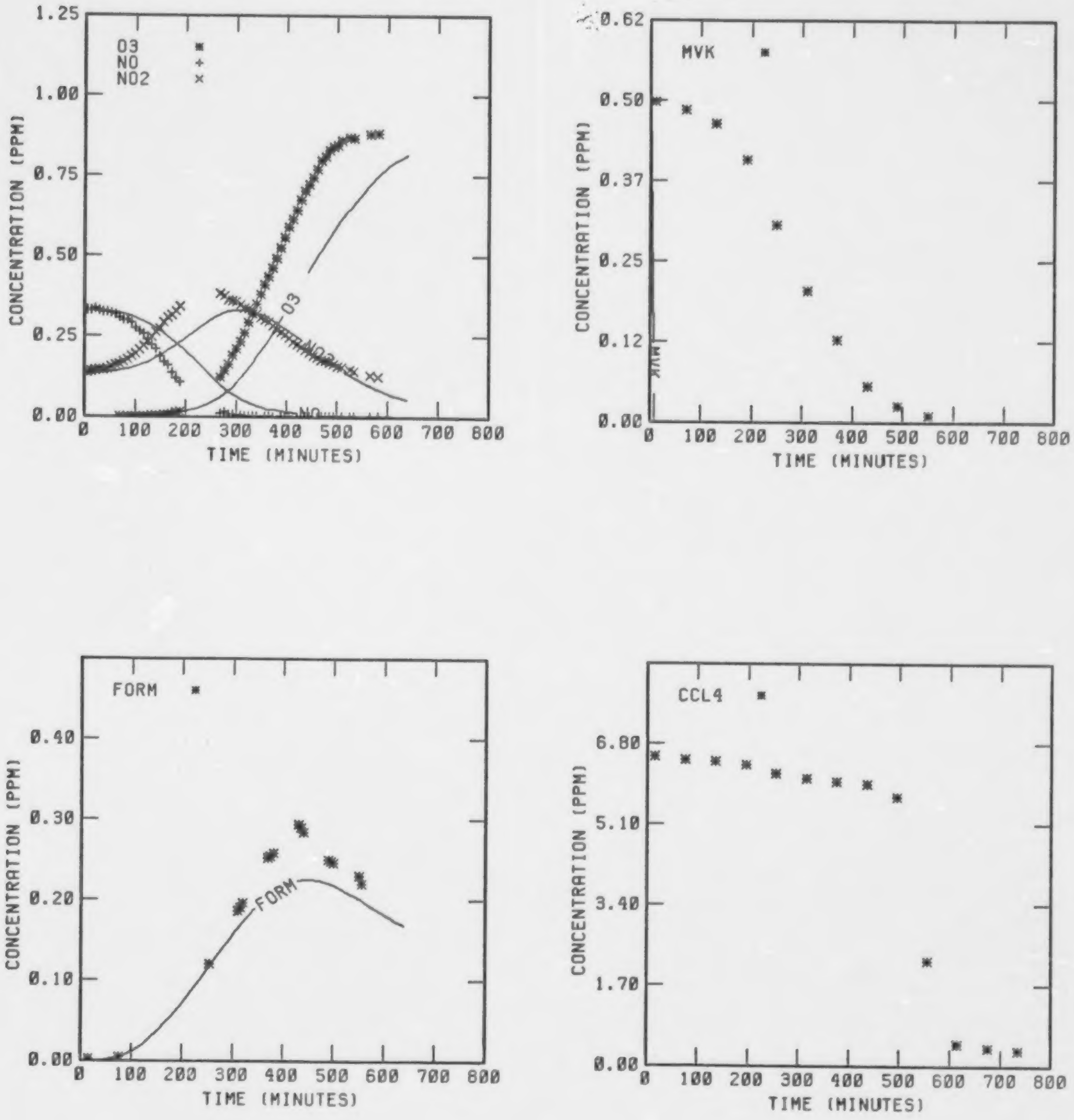

FIGURE B-14. SIMULATION RESULTS FOR UNCR 81381

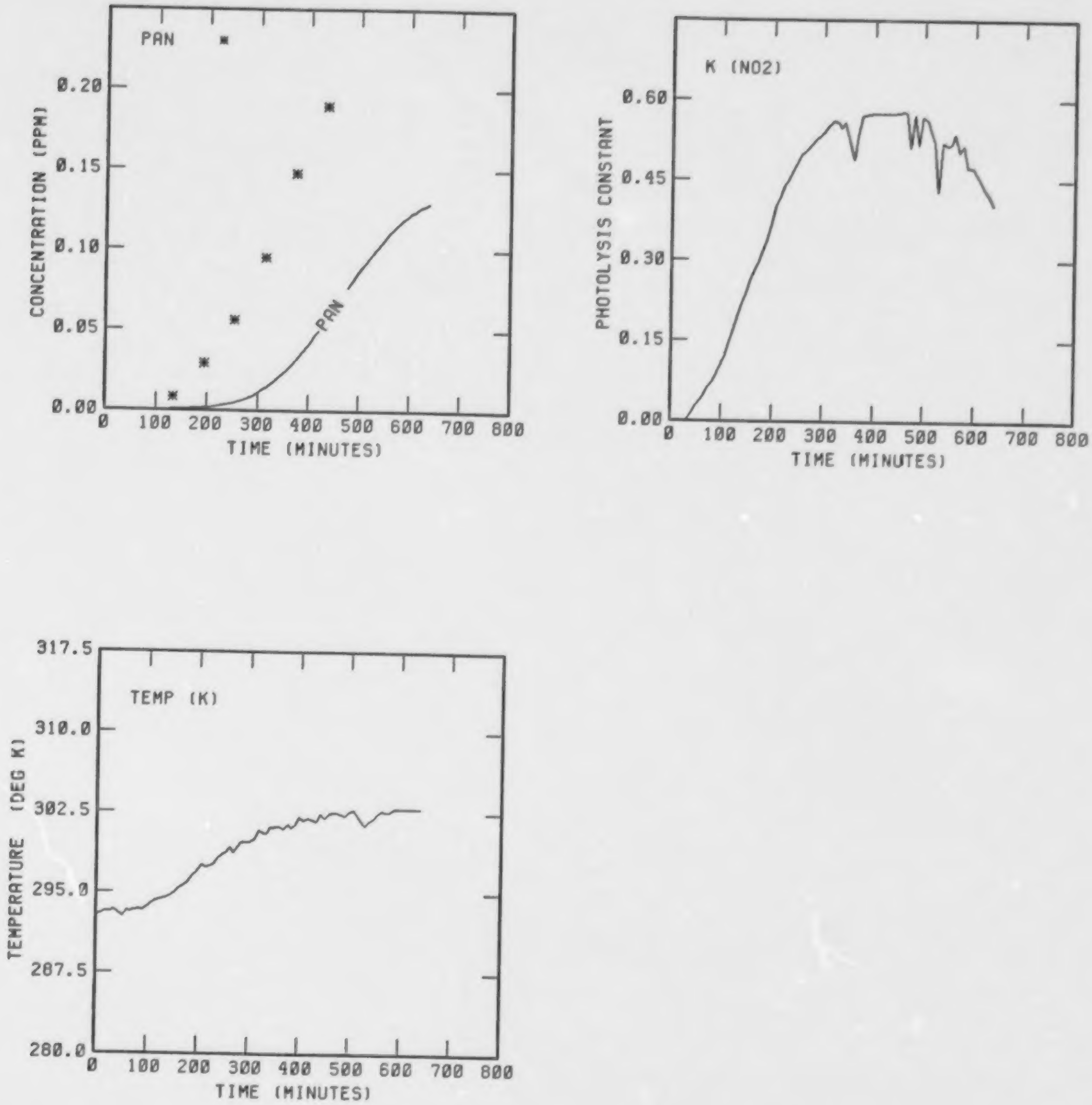

FIGURE B-14. SIMULATION RESULTS FOR
UNCR 81381

(concluded)

Appendix C

SIMULATION RESULTS FOR THE UCR OUTDOOR EXPERIMENTS

TABLE C-1. INITIAL CONDITIONS USED TO SIMULATE THE UCR OUTDOOR CHAMBER EXPERIMENTS

Run No.	NO (ppm)	NO_2 (ppm)	HNO_3 (ppm)	H_2O (ppm)	Isobutene (ppm)	Toluene (ppm)	M-xylene (ppm)	PAR (ppm)	OLE (ppm)	Ethene (ppm)	FORM (ppm)	ALD2 (ppm)	Acetone (ppm)	Injections NO (ppm)
70783R	0.339	0.113	0.011	1.0E+4	0.157	0.067	0.048	2.073	0.081	0.118	0.020	0.000	0.000	-
72783R	0.260	0.120	0.012	2.0E+4	0.326	0.125	0.090	3.992	0.162	0.210	0.001	0.010	0.004	-
72783B	0.270	0.090	0.010	2.0E+3	0.150	0.064	0.051	1.944	0.074	0.107	0.001	0.020	0.005	-
80283R	0.250	0.160	0.009	3.0E+3	0.067	0.035	0.025	0.956	0.036	0.062	0.000	0.150	0.020	-
80283B	0.250	0.163	0.009	2.5E+3	0.144	0.070	0.056	2.124	0.078	0.122	0.060	0.087	0.011	-
82483R	0.225	0.140	0.012	4.0E+3	0.130	0.064	0.048	1.740	0.068	0.108	0.010	0.100	0.010	-
82483B	0.540	0.220	0.015	3.0E+3	0.133	0.070	0.056	1.707	0.070	0.109	0.040	0.050	0.005	-
83083R	0.480	0.260	0.015	9.0E+3	0.260	0.061	0.049	2.613	0.145	0.220	0.100	0.060	0.007	-
83083B	0.120	0.270	0.008	8.0E+3	0.125	0.060	0.048	1.840	0.070	0.109	0.050	0.085	0.007	-
90783R	0.270	0.090	0.007	5.0E+3	0.140	0.053	0.046	1.853	0.071	0.104	0.003	0.120	0.007	-
90783B	0.270	0.090	0.005	5.0E+3	0.141	0.053	0.046	1.853	0.074	0.104	0.010	0.100	0.007	0.170 (day 2)
92183R	0.640	0.075	0.015	4.0E+3	0.200	0.125	0.096	3.496	0.110	0.185	0.010	0.120	0.010	-
92183B	0.330	0.065	0.004	3.0E+3	0.120	0.062	0.055	1.817	0.068	0.090	0.020	0.100	0.010	-
92883R	0.310	0.080	0.003	5.0E+3	0.136	0.052	0.045	1.870	0.076	0.092	0.008	0.125	0.003	-
92883B	0.150	0.030	0.002	5.0E+3	0.140	0.054	0.045	1.863	0.080	0.091	0.030	0.125	0.005	-
100483R	0.298	0.075	0.006	2.0E+3	0.135	0.053	0.045	1.881	0.073	0.090	0.063	0.135	0.011	0.140 (day 3)
100483B	0.130	0.040	0.003	2.0E+3	0.131	0.054	0.045	1.926	0.070	0.090	0.030	0.120	0.010	0.140 (day 3)

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TABLE C-1. (concluded)

Run No.	NO (ppm)	NO_2 (ppm)	HNO_3 (ppm)	H_2O (ppm)	Isobutene (ppm)	Toluene (ppm)	M-xylene (ppm)	PAR (ppm)	OLE (ppm)	Ethene (ppm)	FORM (ppm)	ALD2 (ppm)	Acetone (ppm)	Injections NO (ppm)
101083B	0.098	0.042	0.003	1.2E+4	0.115	0.055	0.040	1.900	0.069	0.142	0.060	0.210	0.020	0.160 (day 2) 0.140 (day 3) 0.080 (day 4)
71283R	0.330	0.085	0.009	7.0E+3	0.137	0.064	0.048	1.880	0.077	0.113	0.000	0.100	0.005	-
71283B	0.330	0.085	0.009	8.0E+3	0.137	0.062	0.048	1.896	0.077	0.112	0.000	0.080	0.004	-
71983R	0.300	0.175	0.013	8.0E+3	0.151	0.070	0.056	2.124	0.082	0.138	0.010	0.060	0.006	-
71983B	0.305	0.195	0.014	8.0E+3	0.149	0.073	0.057	2.066	0.080	0.138	0.050	0.080	0.006	0.160 (day 2)

The only chamber dependent modifications to the CBM-XR mechanism where the use of an ozone decay constant of 1.25×10^{-4} min^{-1}, an appearance of HNO_2 at 1×10^{-4} ppm min^{-1}, and change in the rate constant for reaction 17 ($N_2O_5 + H_2O$) to 1.5×10^{-5} ppm^{-1} min^{-1}.

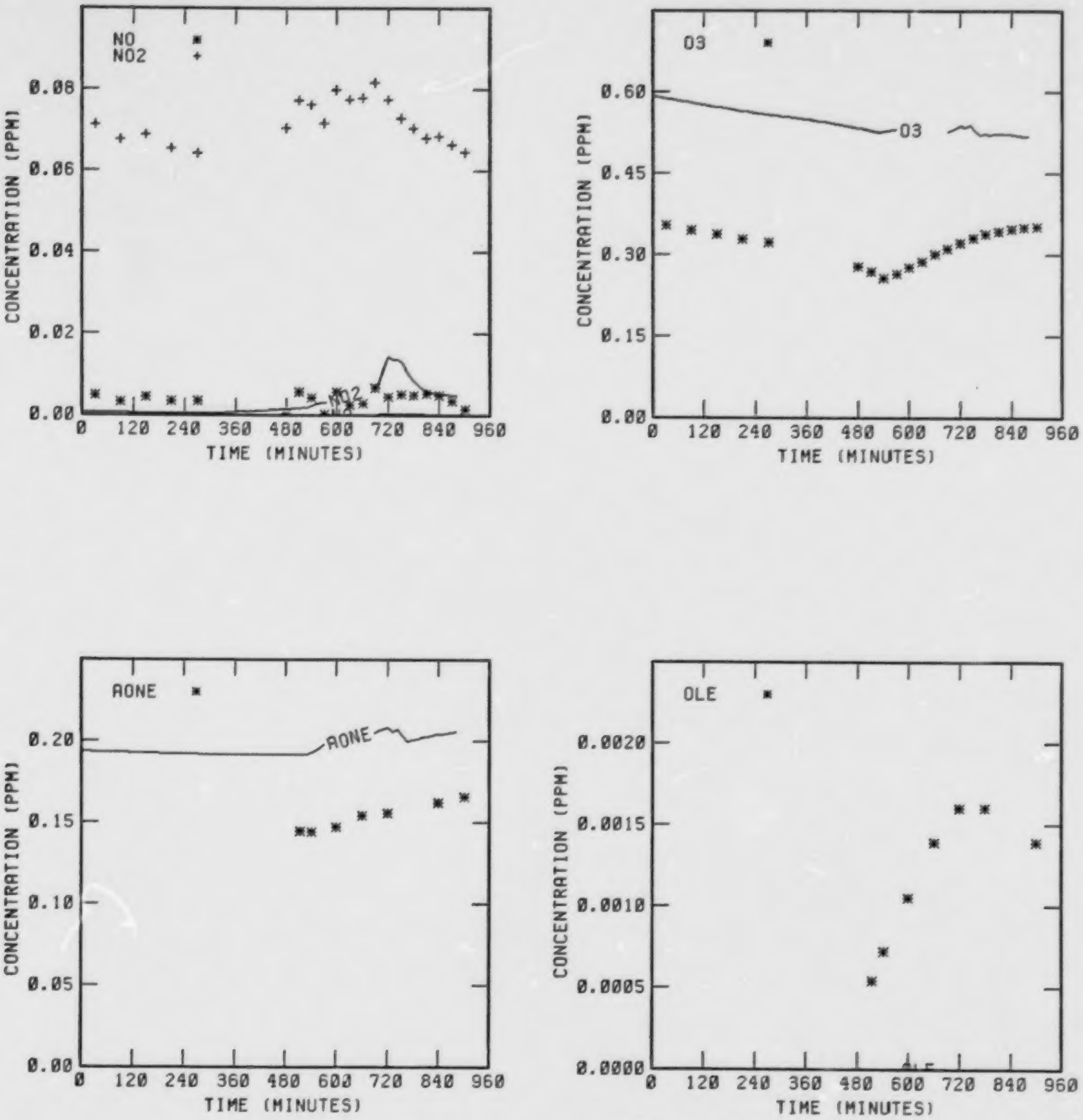


FIGURE C- 1. SIMULATION RESULTS FOR OTCR.70883

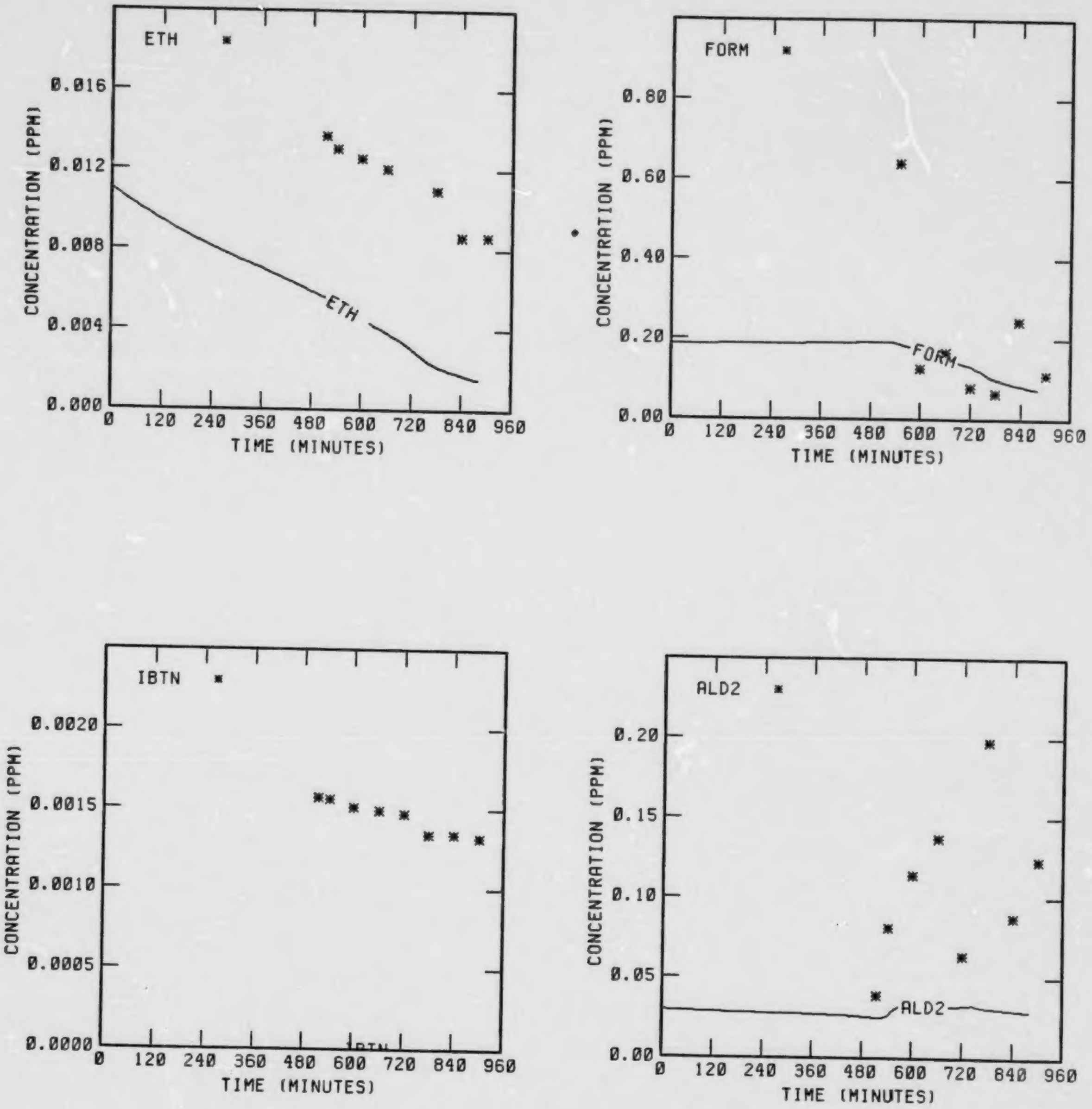


FIGURE C-1 . SIMULATION RESULTS FOR OTCR.70883 (continued).

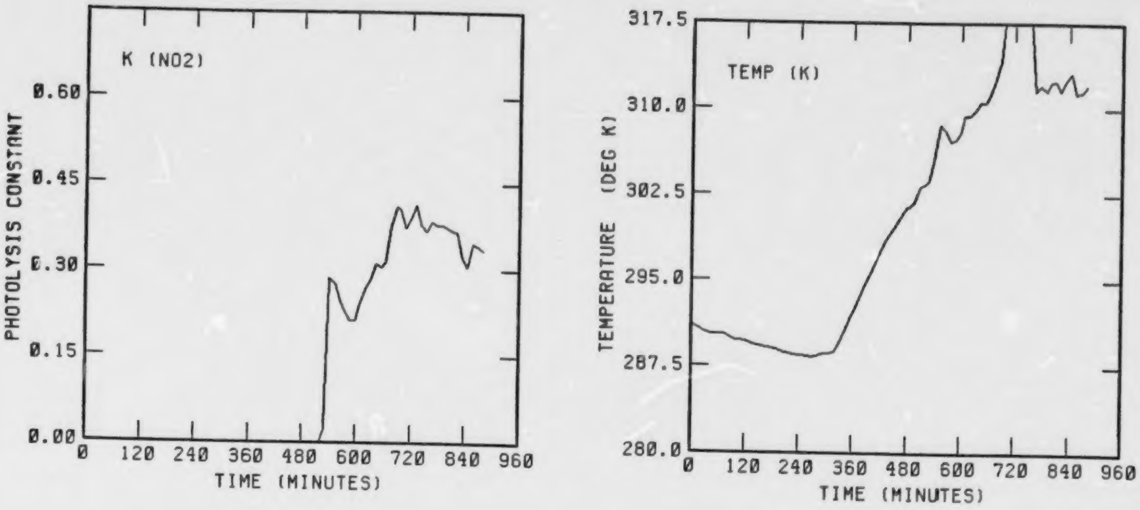


FIGURE C-1. SIMULATION RESULTS FOR
OTCR.70883
(continued).

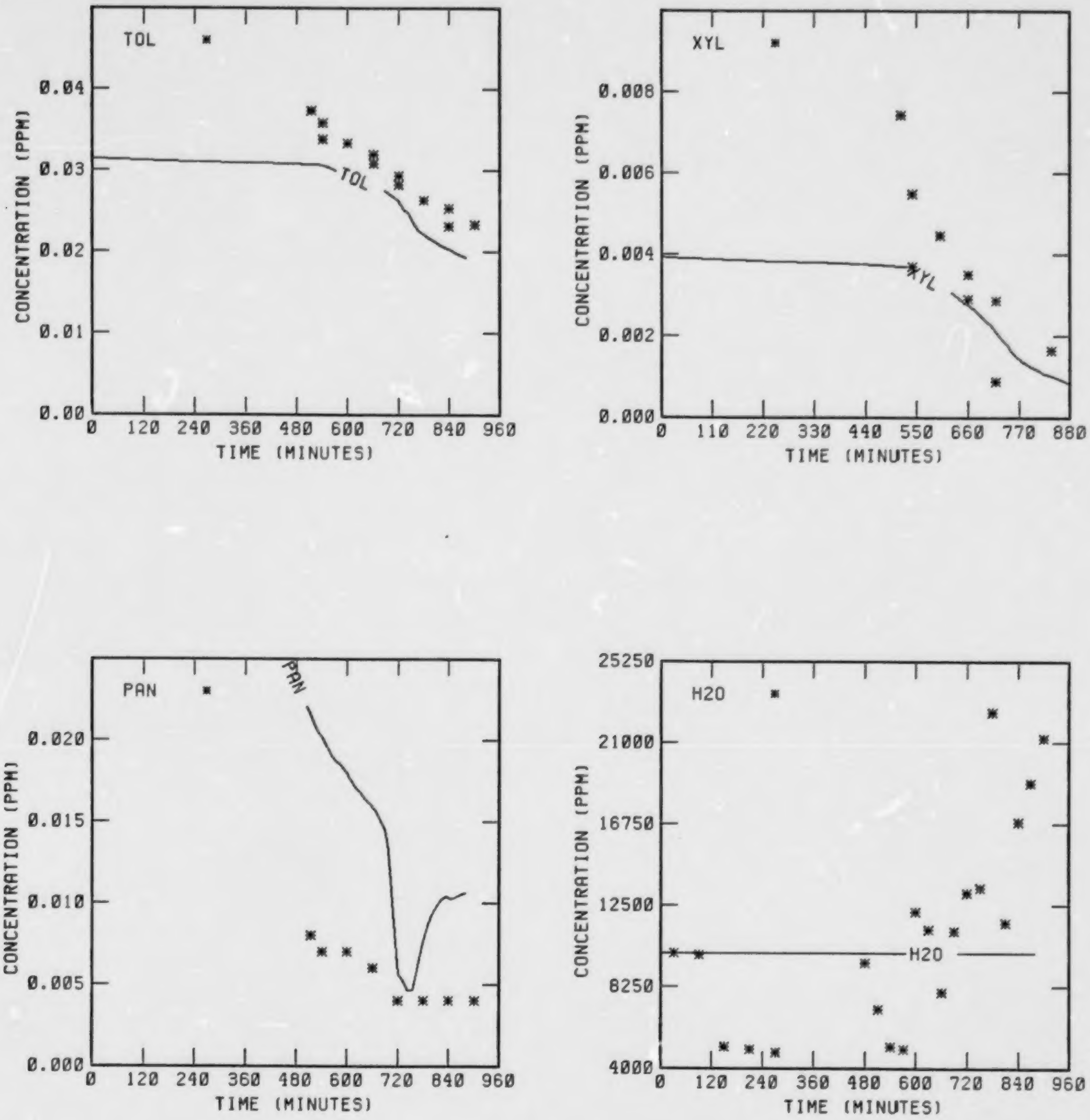


FIGURE C-1. SIMULATION RESULTS FOR
OTCR.70883

(concluded).

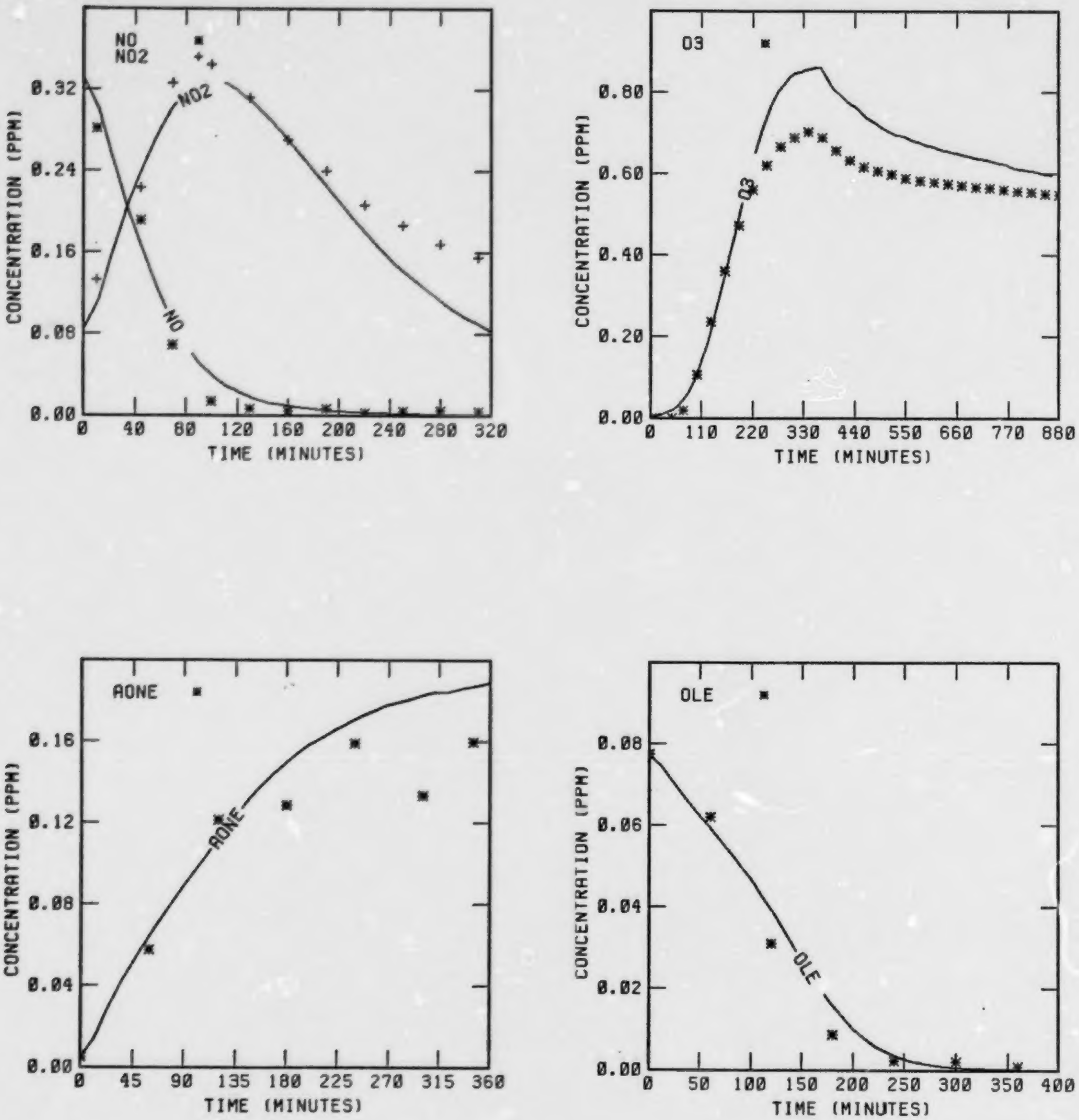


FIGURE C-2. SIMULATION RESULTS FOR OTCR.71283

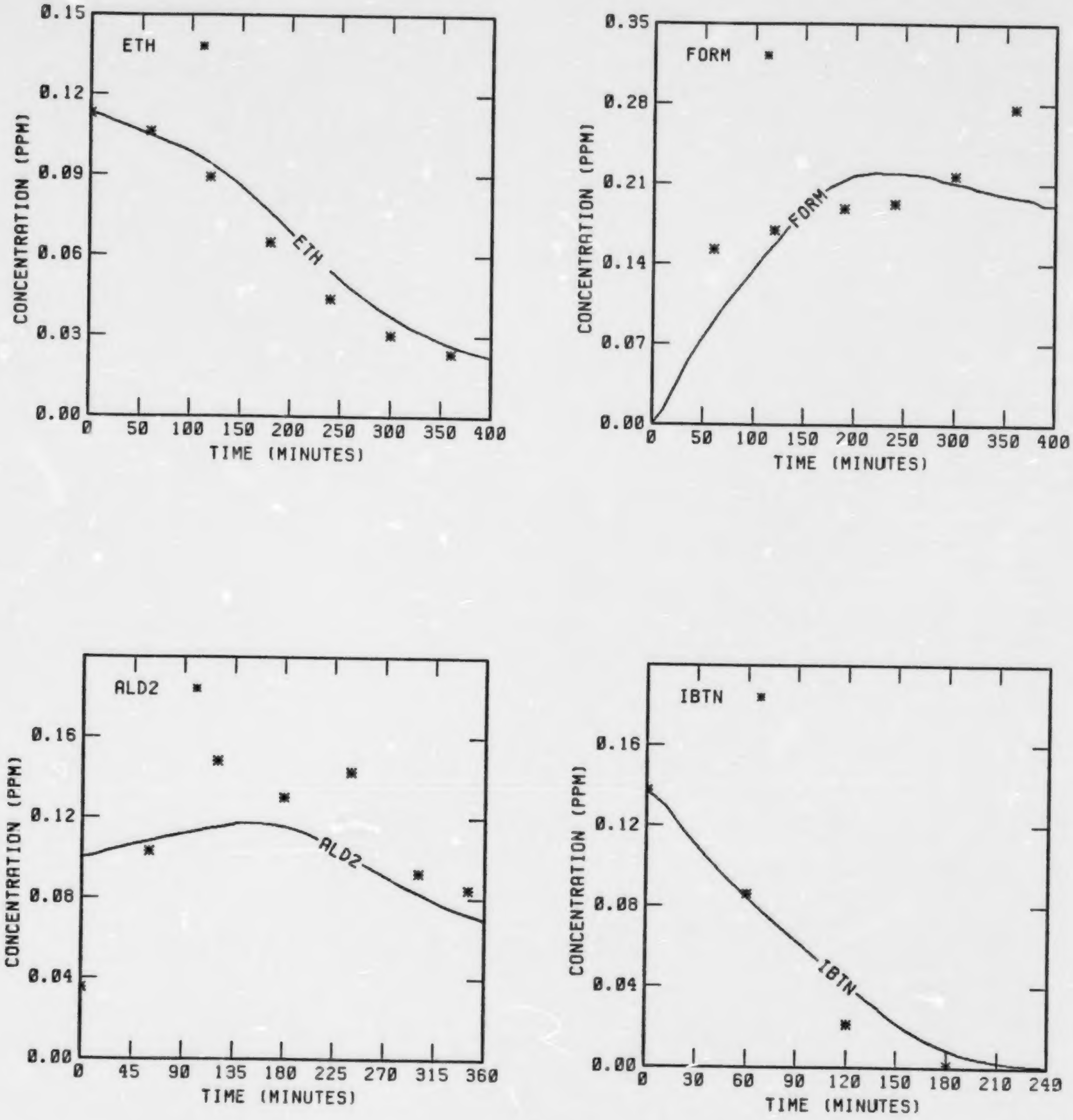


FIGURE C-2. SIMULATION RESULTS FOR
OTCR.71283
(continued).

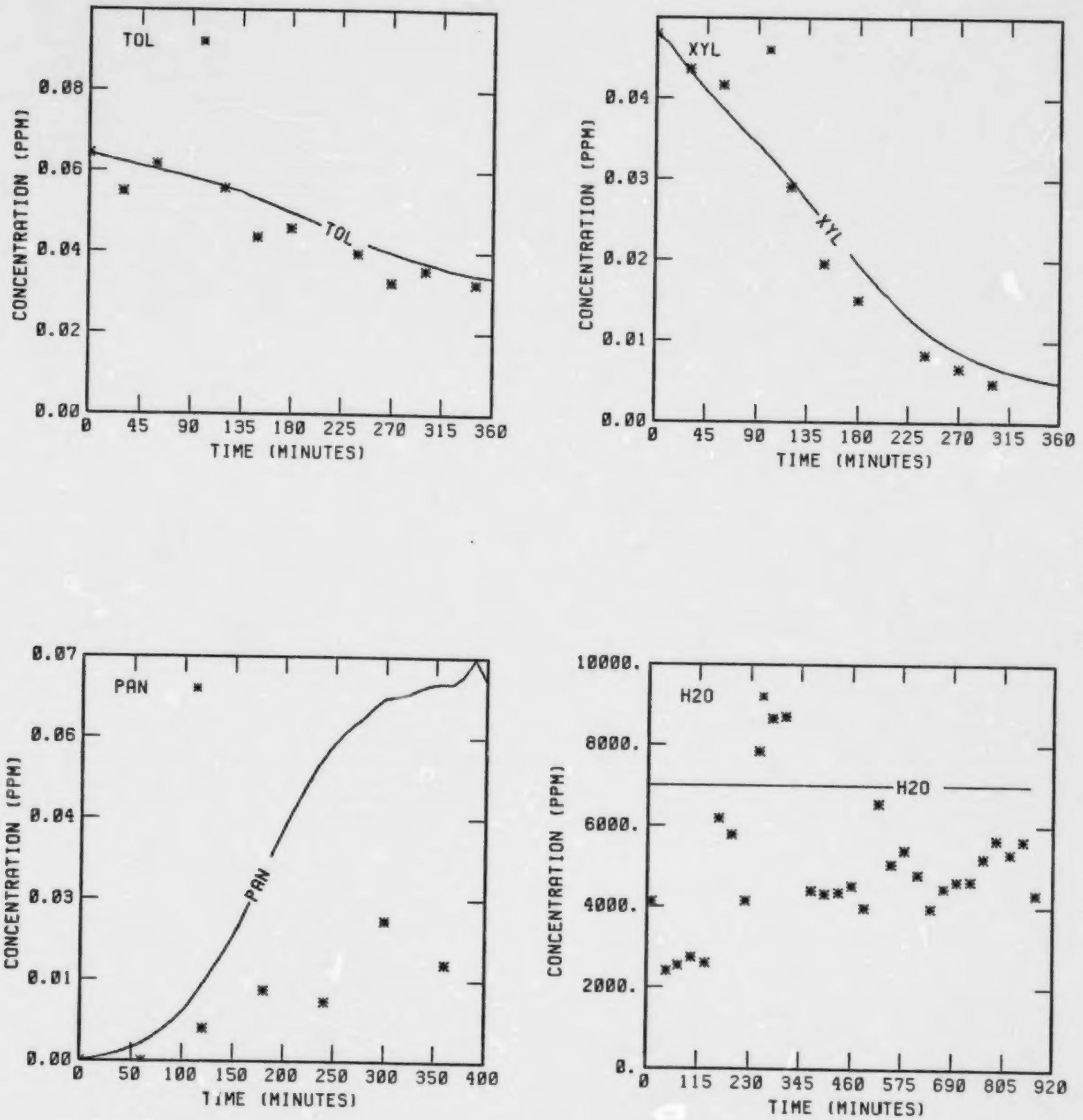


FIGURE C-2 . SIMULATION RESULTS FOR
OTCR.71283
(continued).

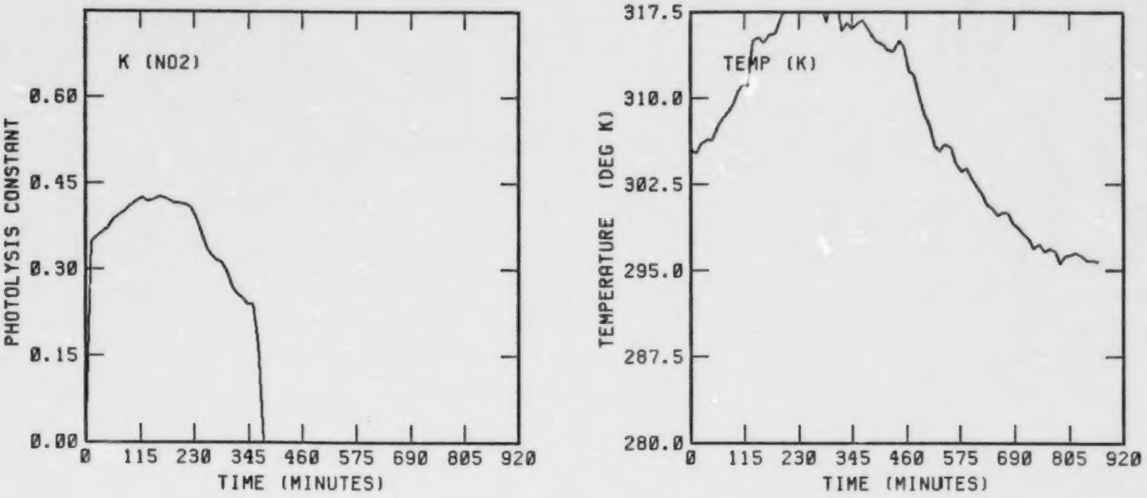


FIGURE C-2 . SIMULATION RESULTS FOR
OTCR.71283
(concluded).

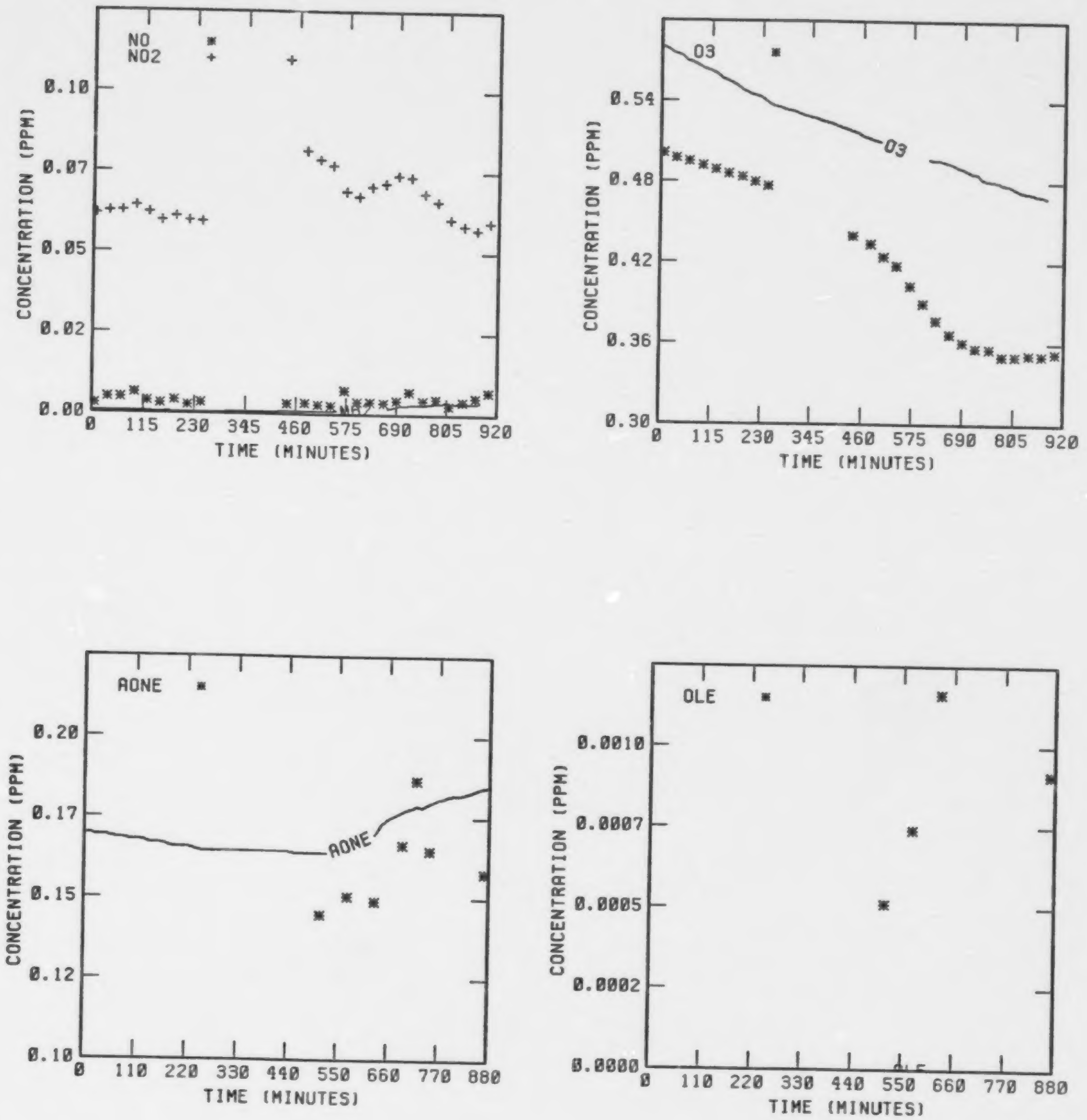


FIGURE C-3. SIMULATION RESULTS FOR
OTCB.71383

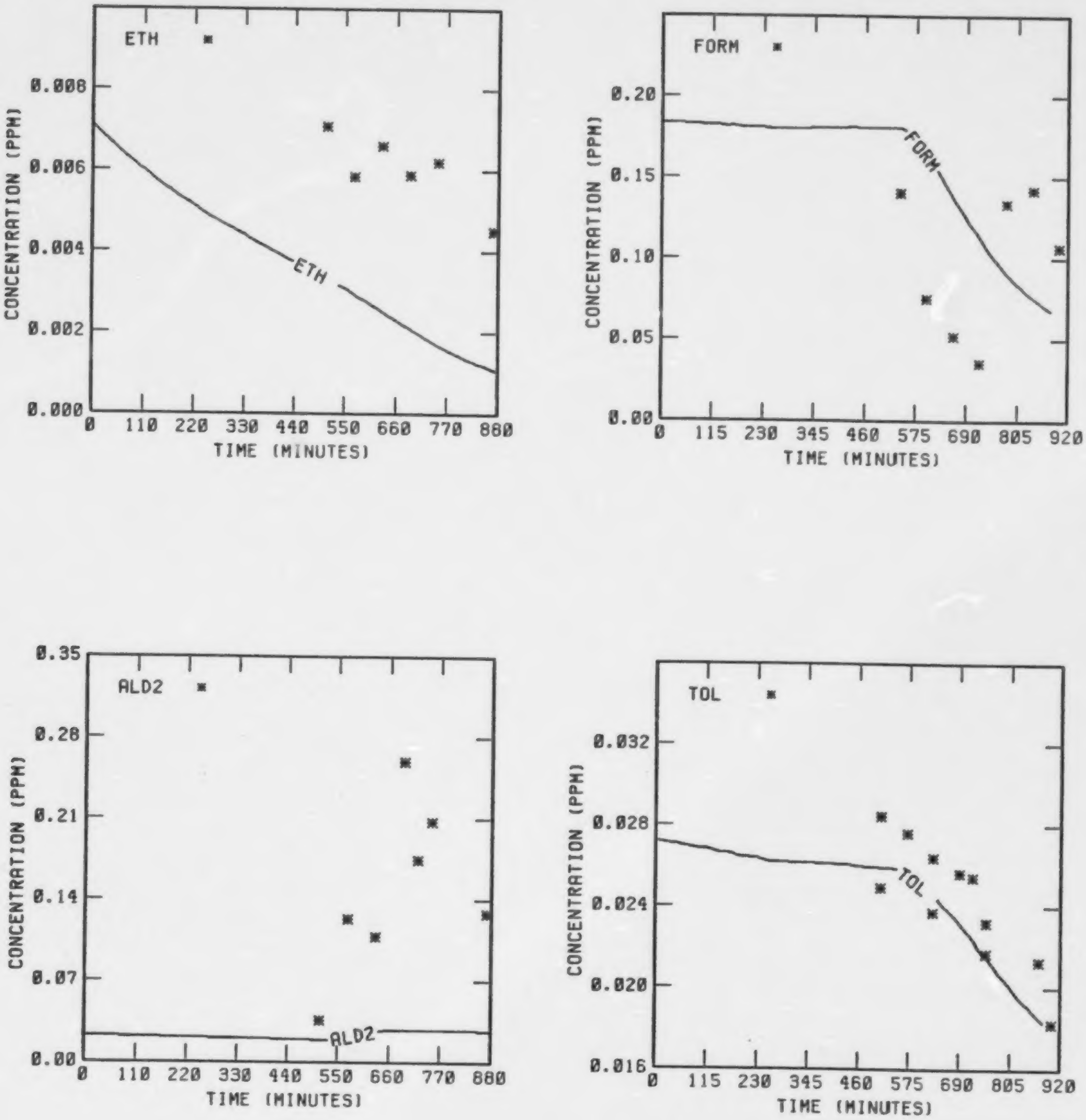


FIGURE C-3 . SIMULATION RESULTS FOR
OTCB.71383
(continued).

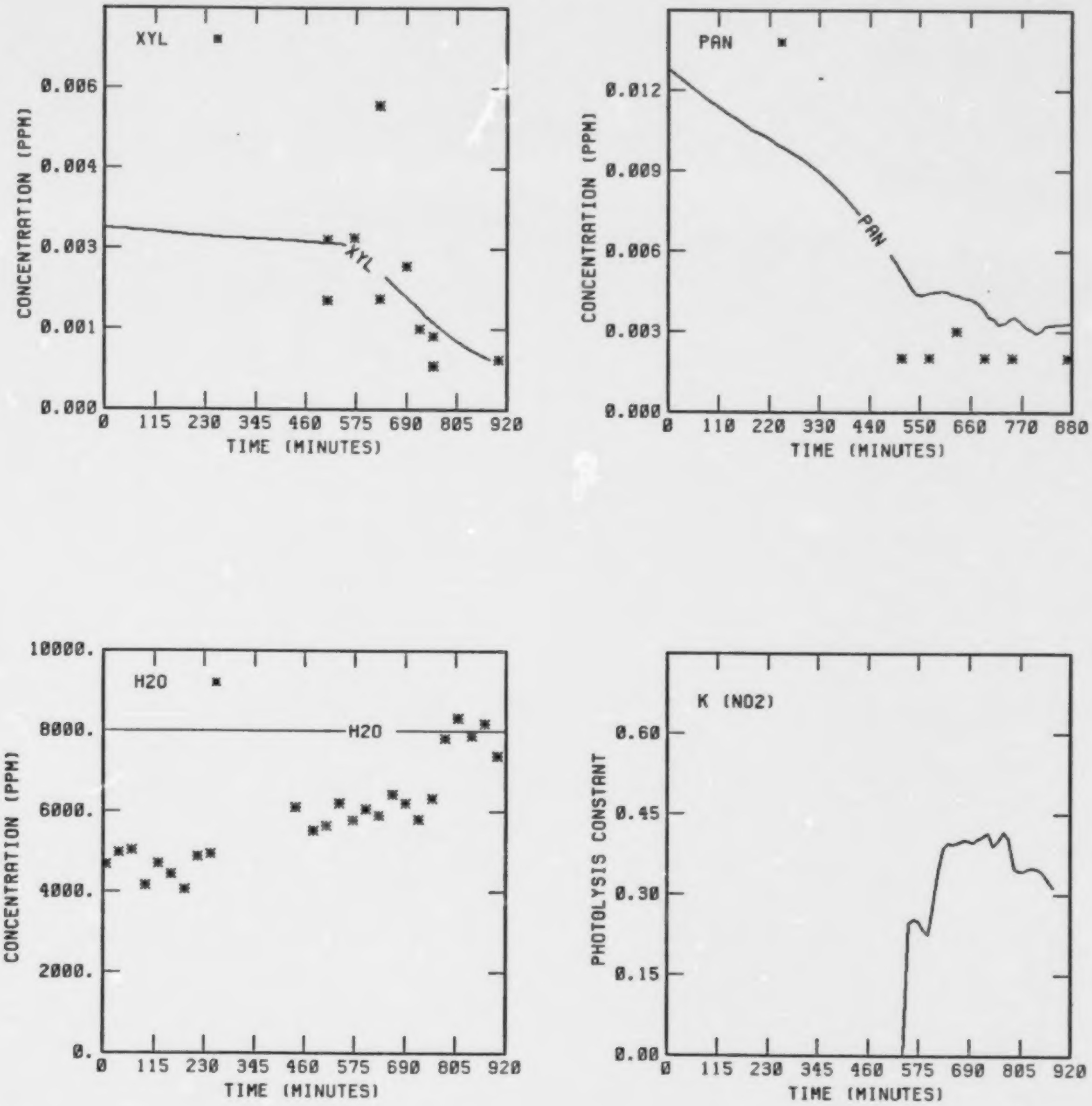


FIGURE C-3. SIMULATION RESULTS FOR
OTCB.71383
(continued).

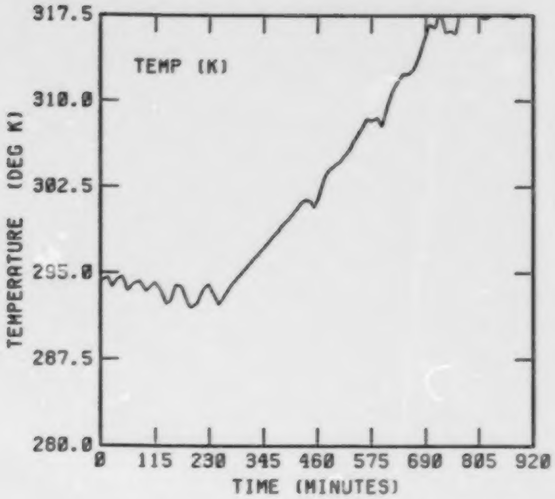


FIGURE C-3 . SIMULATION RESULTS FOR
OTCB.71383

(concluded).

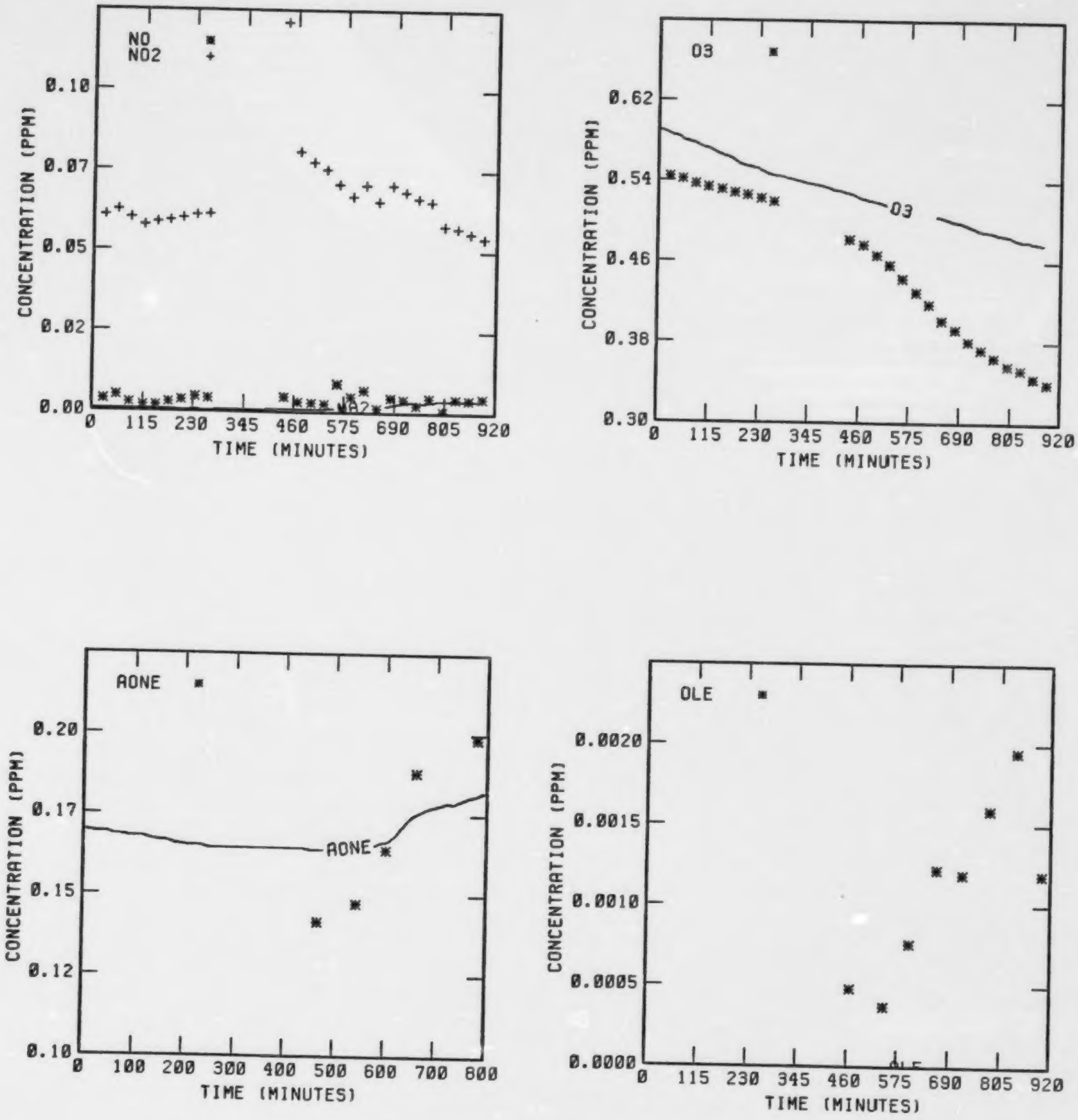


FIGURE C-4. SIMULATION RESULTS FOR
OTCR.71383

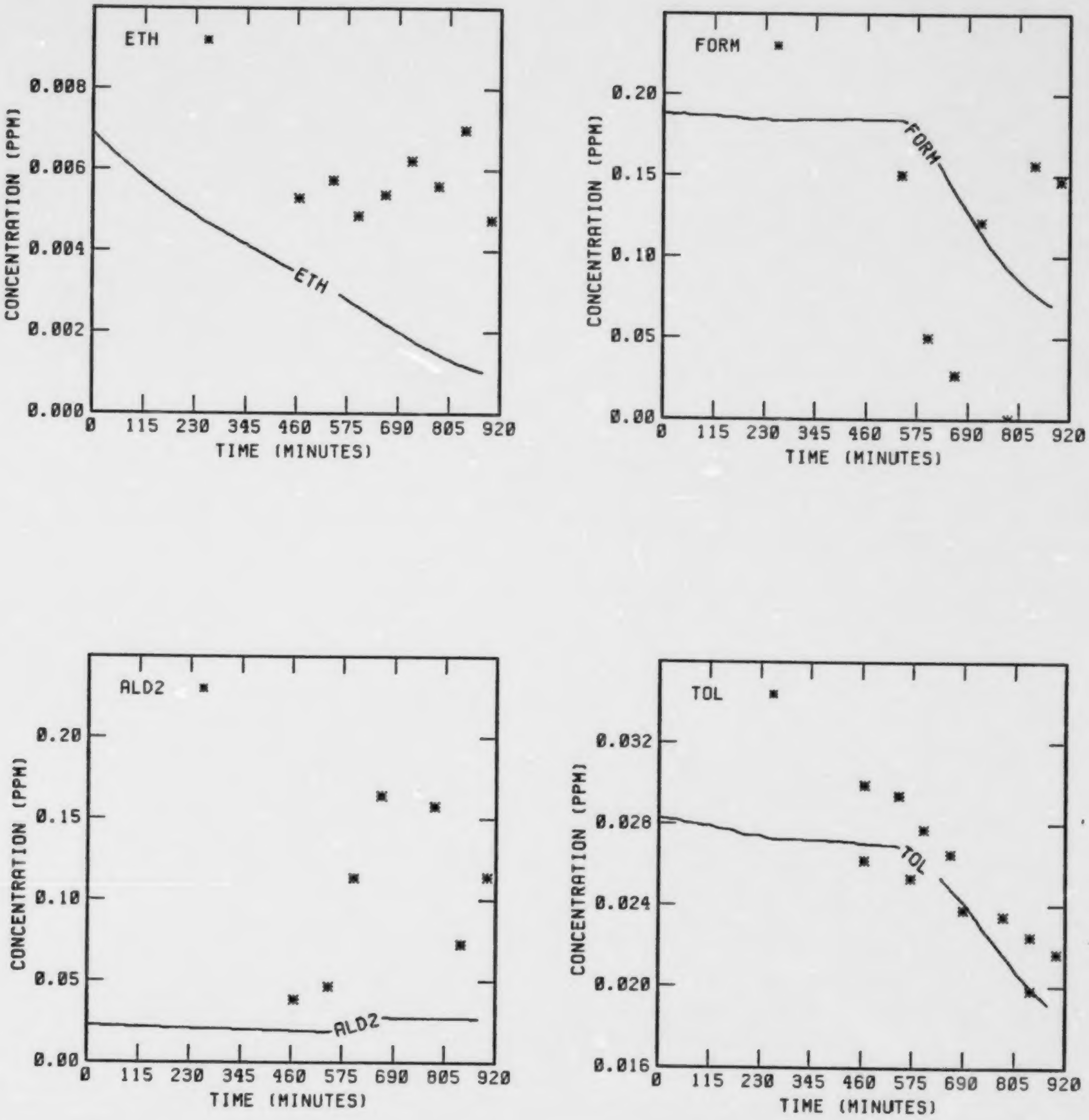


FIGURE C-4. SIMULATION RESULTS FOR OTCR.71383

(continued).

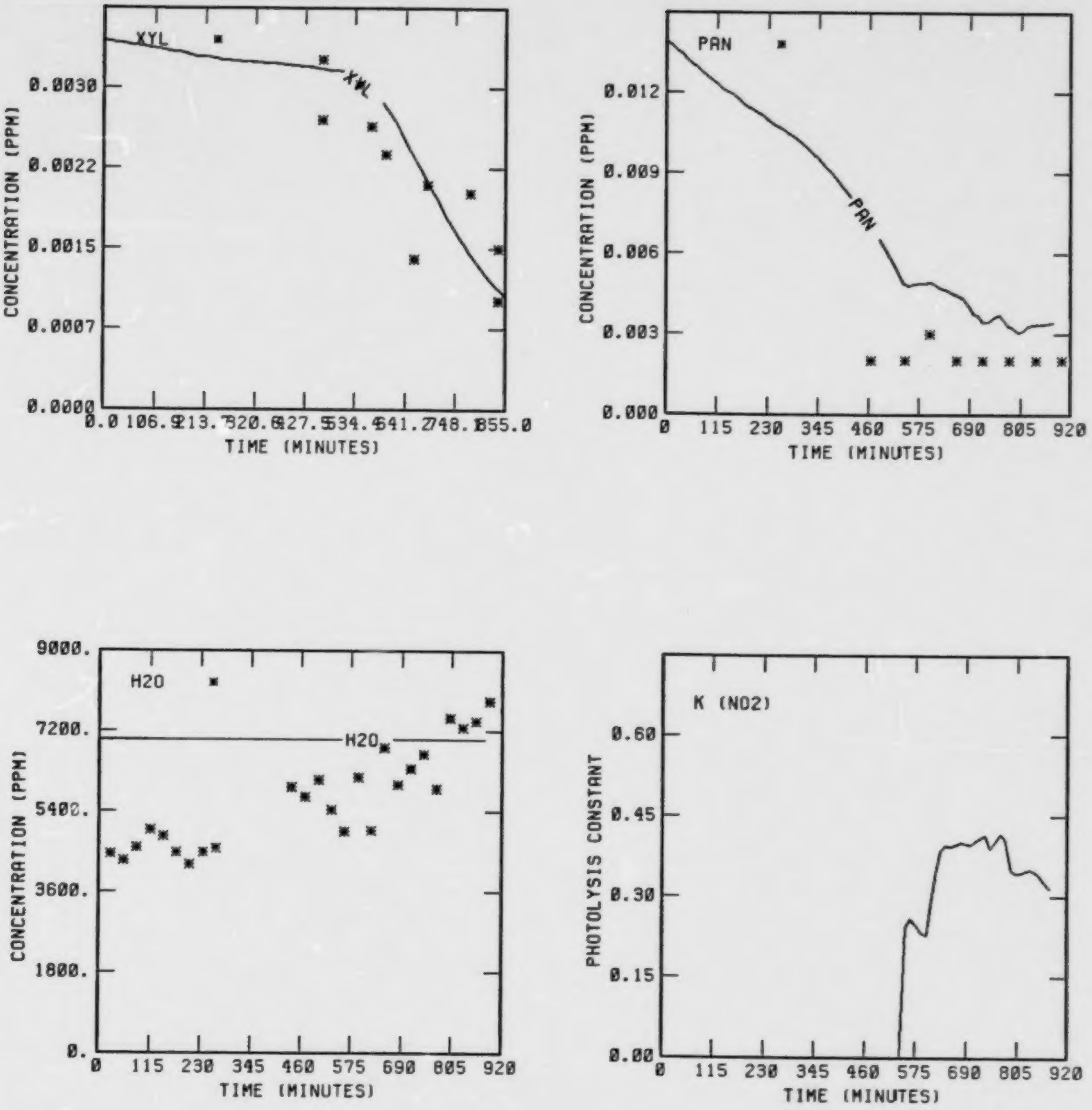


FIGURE C-4. SIMULATION RESULTS FOR
OTCR.71383

(continued).

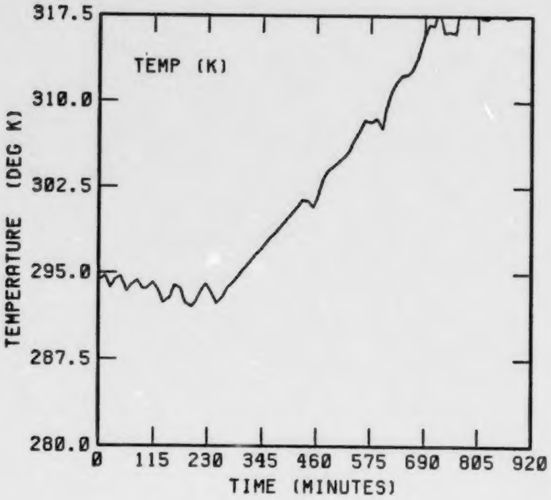


FIGURE C-4. SIMULATION RESULTS FOR OTCR.71383 (concluded).

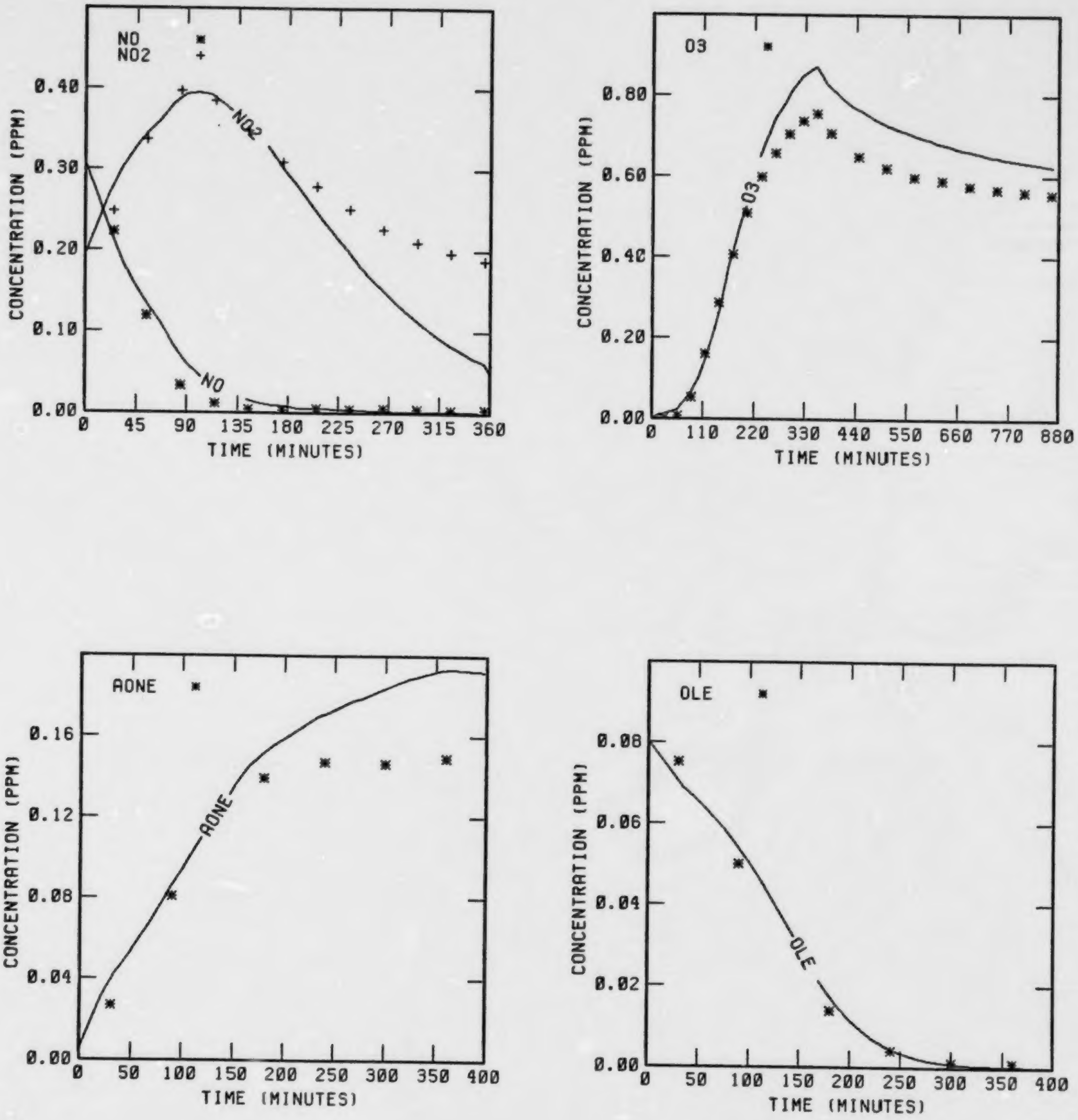


FIGURE C-5. SIMULATION RESULTS FOR
OTCB.71983

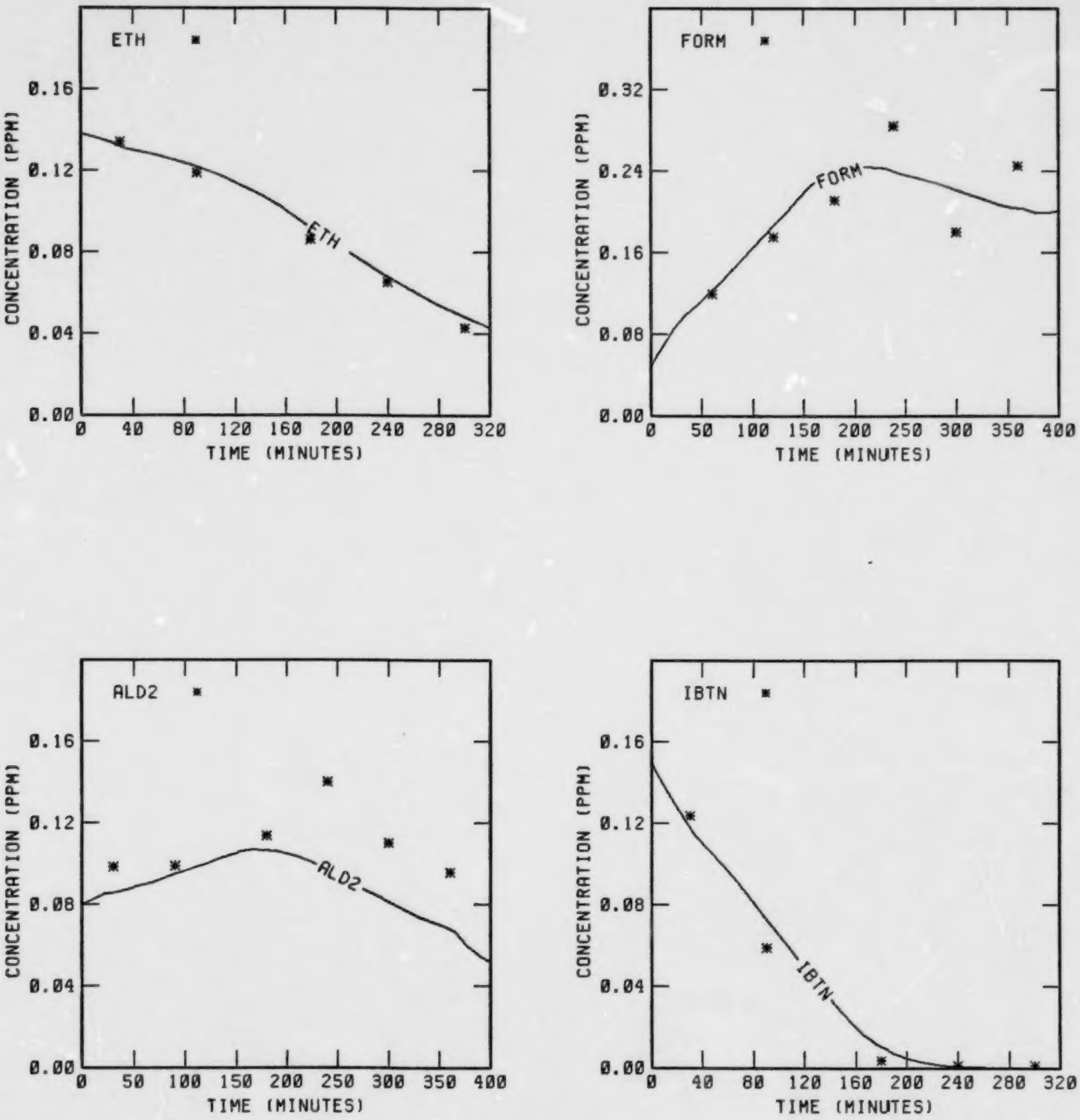


FIGURE C-5. SIMULATION RESULTS FOR OTCB.71983 (continued).

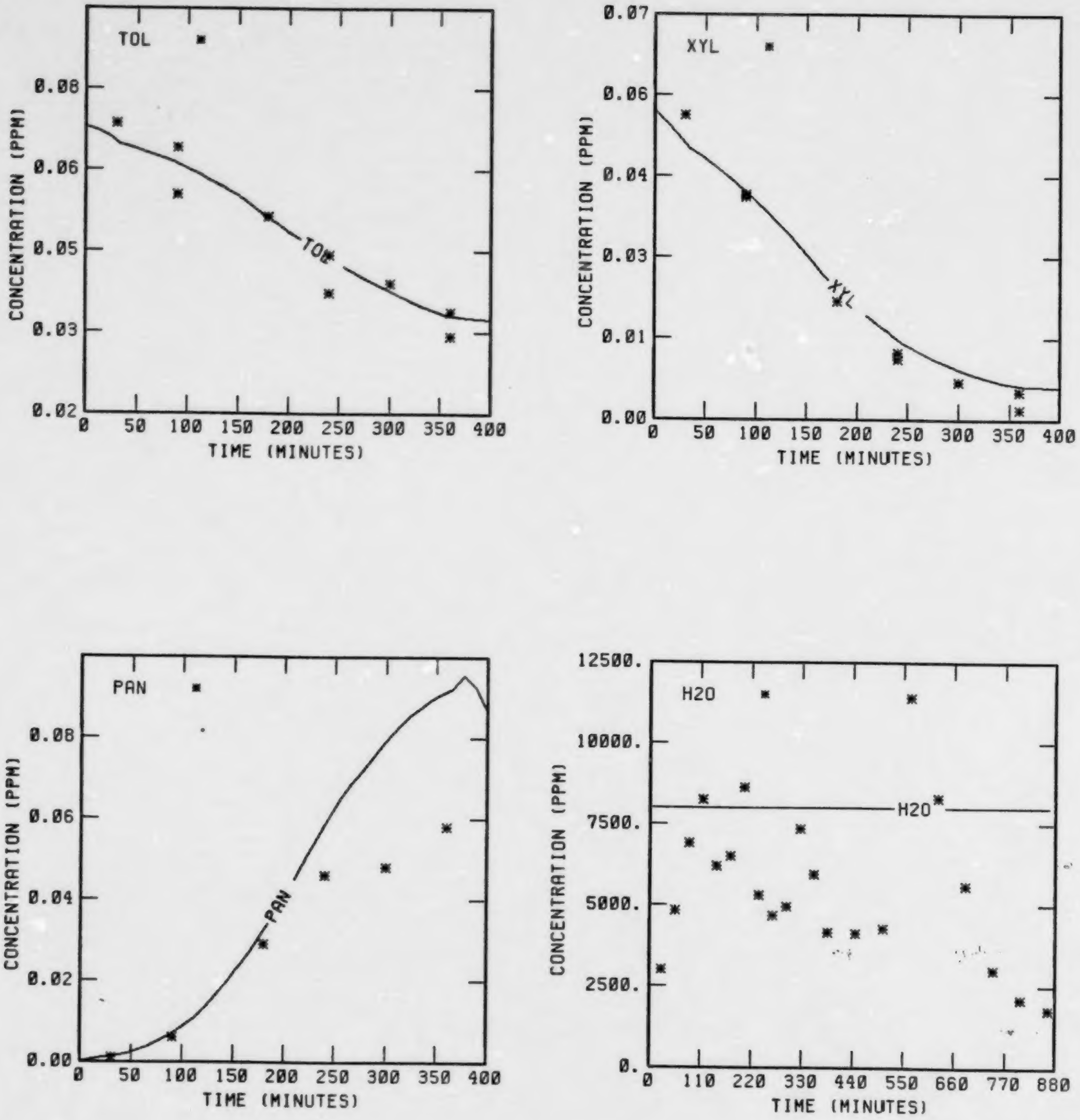


FIGURE C-5. SIMULATION RESULTS FOR OTCB.71983 (continued).

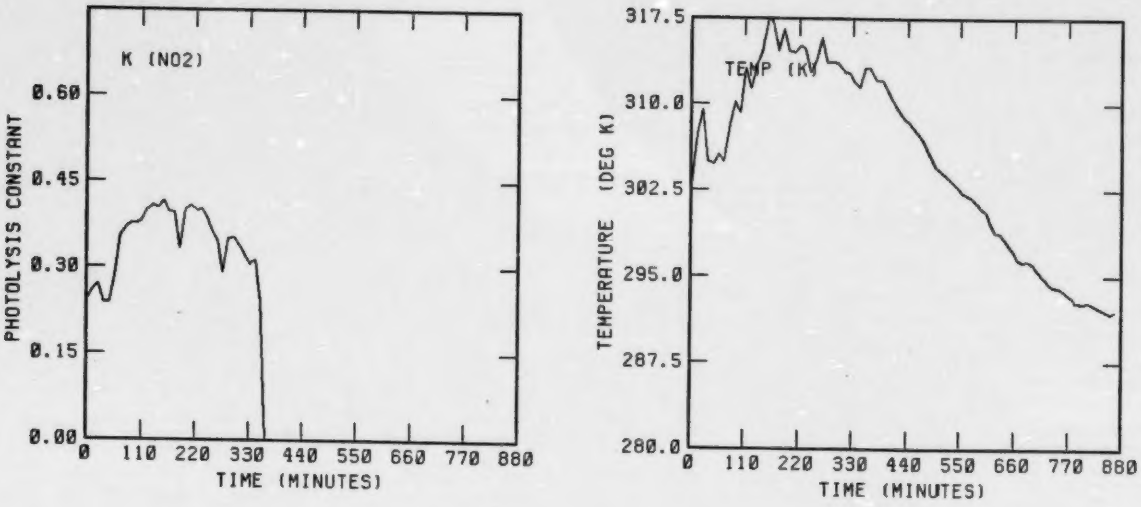


FIGURE C-5. SIMULATION RESULTS FOR OTCB.71983

(concluded).

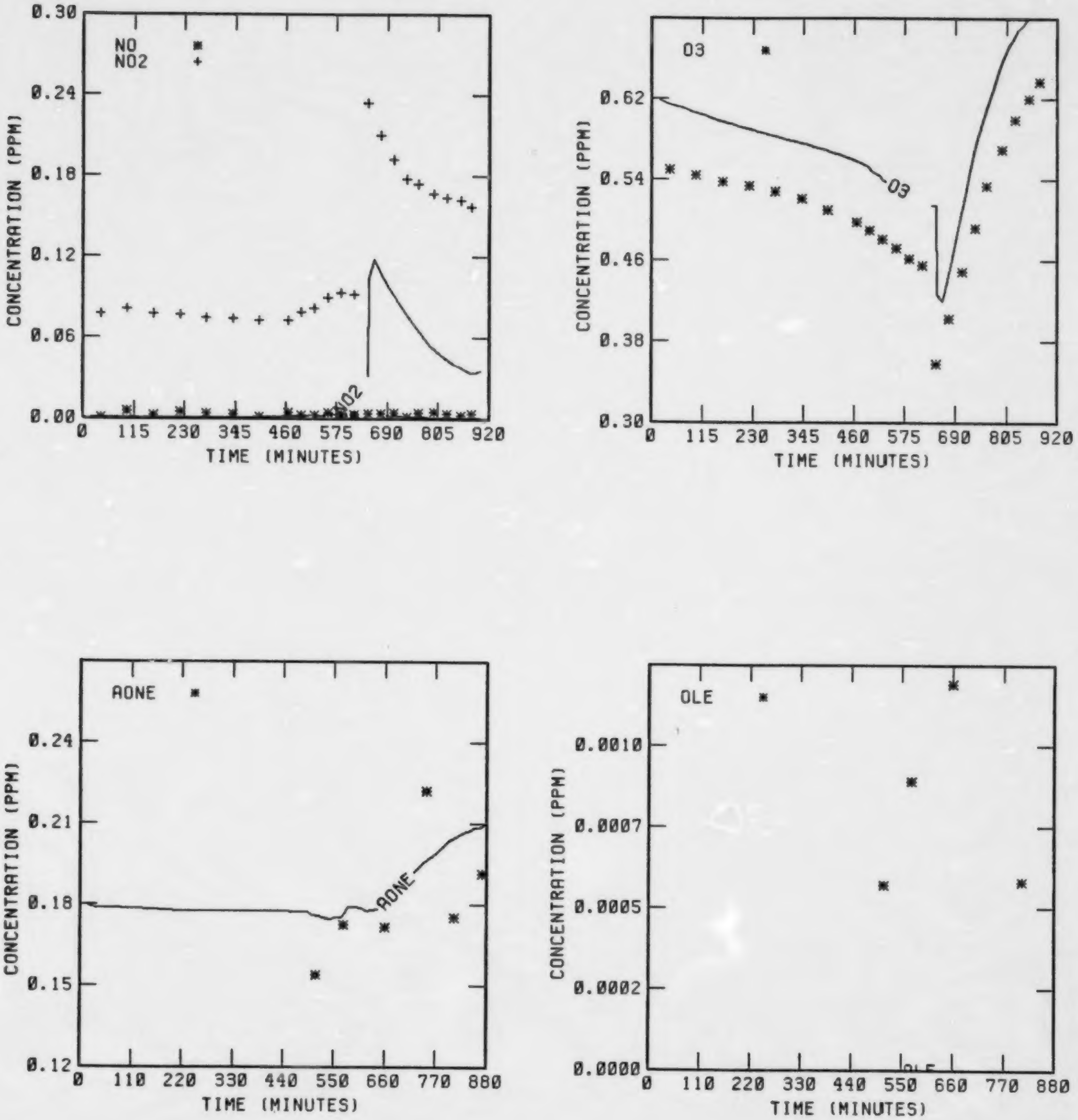


FIGURE C-6. SIMULATION RESULTS FOR
OTCB.72083

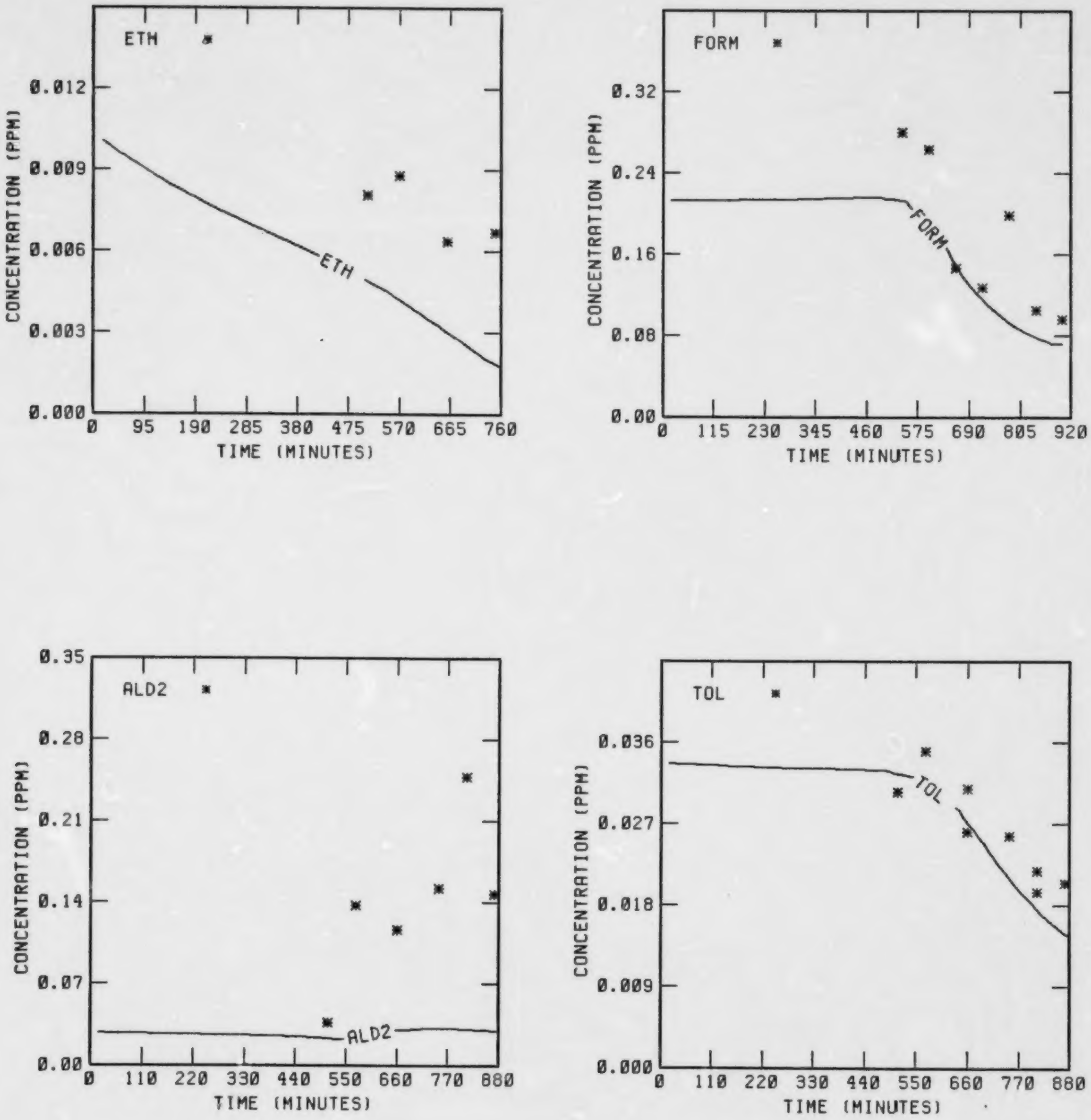


FIGURE C-6. SIMULATION RESULTS FOR
OTCB.72083
(continued).

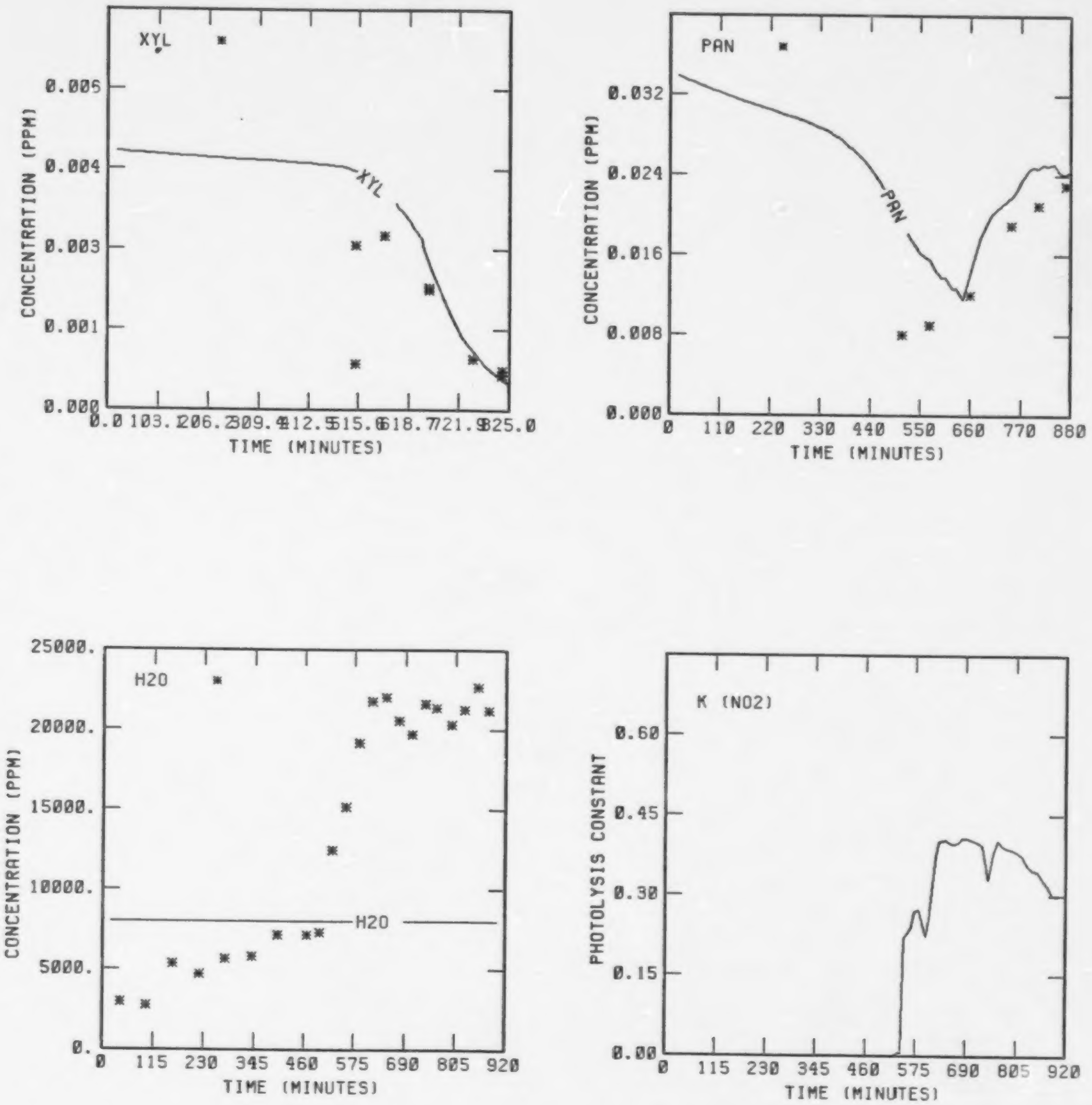


FIGURE C-6. SIMULATION RESULTS FOR
OTCB.72083

(continued).

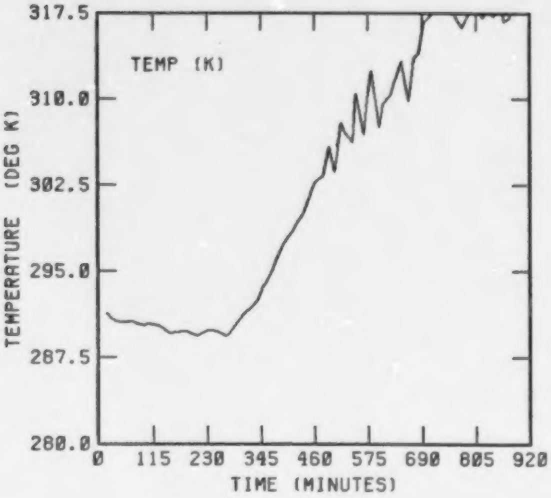


FIGURE C-6. SIMULATION RESULTS FOR
OTCB.72083

(concluded).

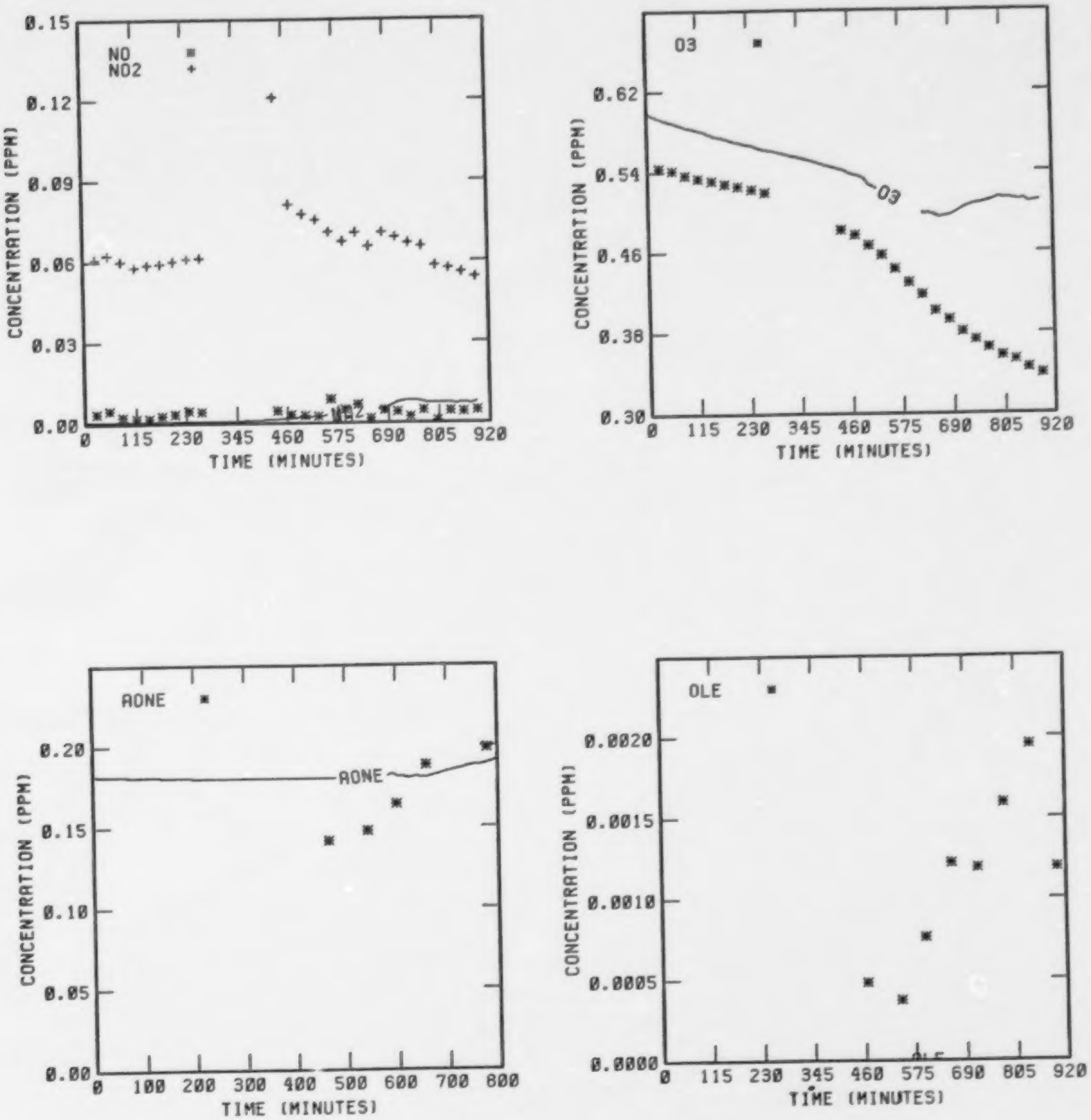


FIGURE C-7 . SIMULATION RESULTS FOR OTCR.72083

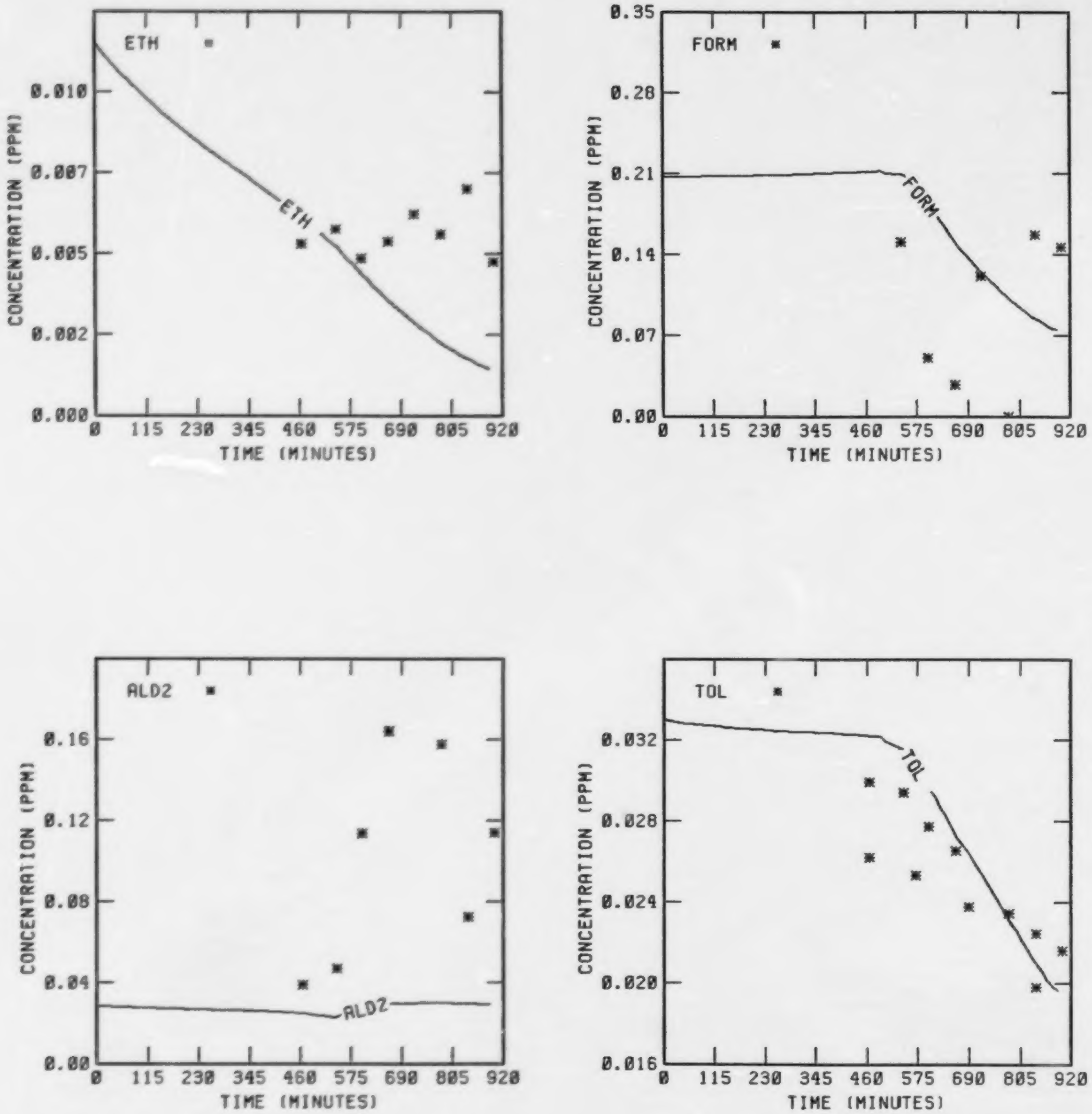


FIGURE C-7. SIMULATION RESULTS FOR
OTCR.72083

(continued).

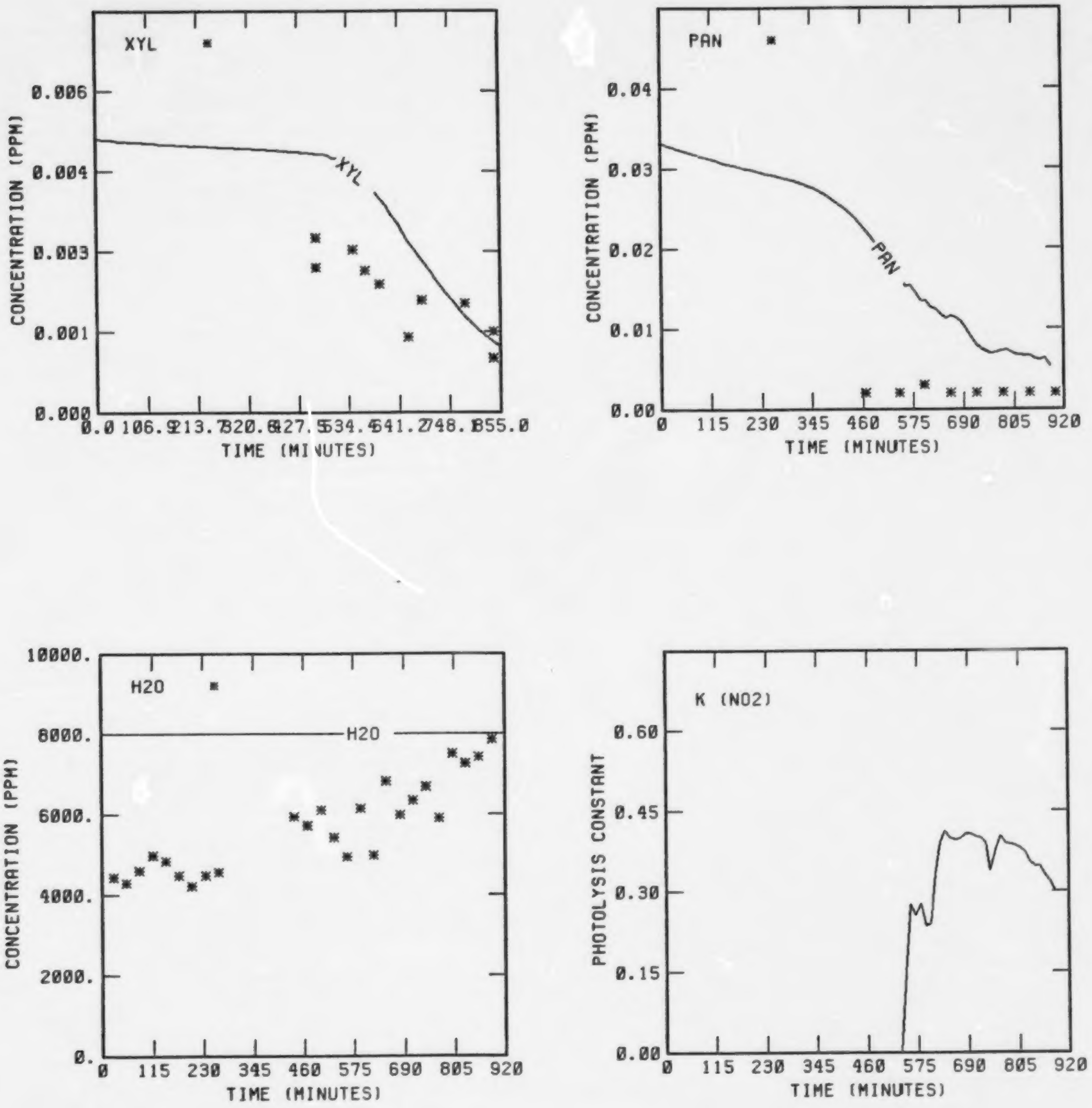


FIGURE C-7. SIMULATION RESULTS FOR
OTCR.72083
(continued).

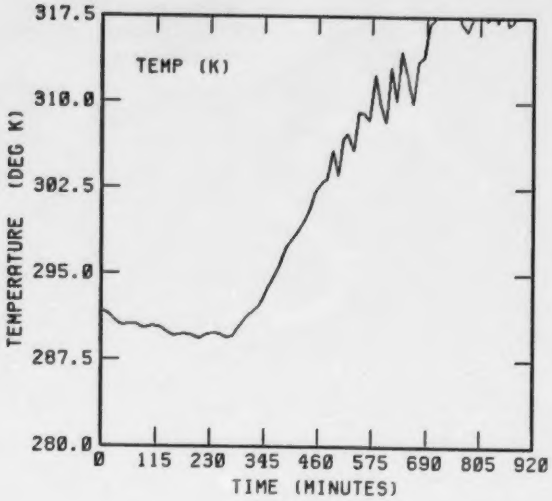


FIGURE C- 7. SIMULATION RESULTS FOR
OTCR.72083
(concluded).

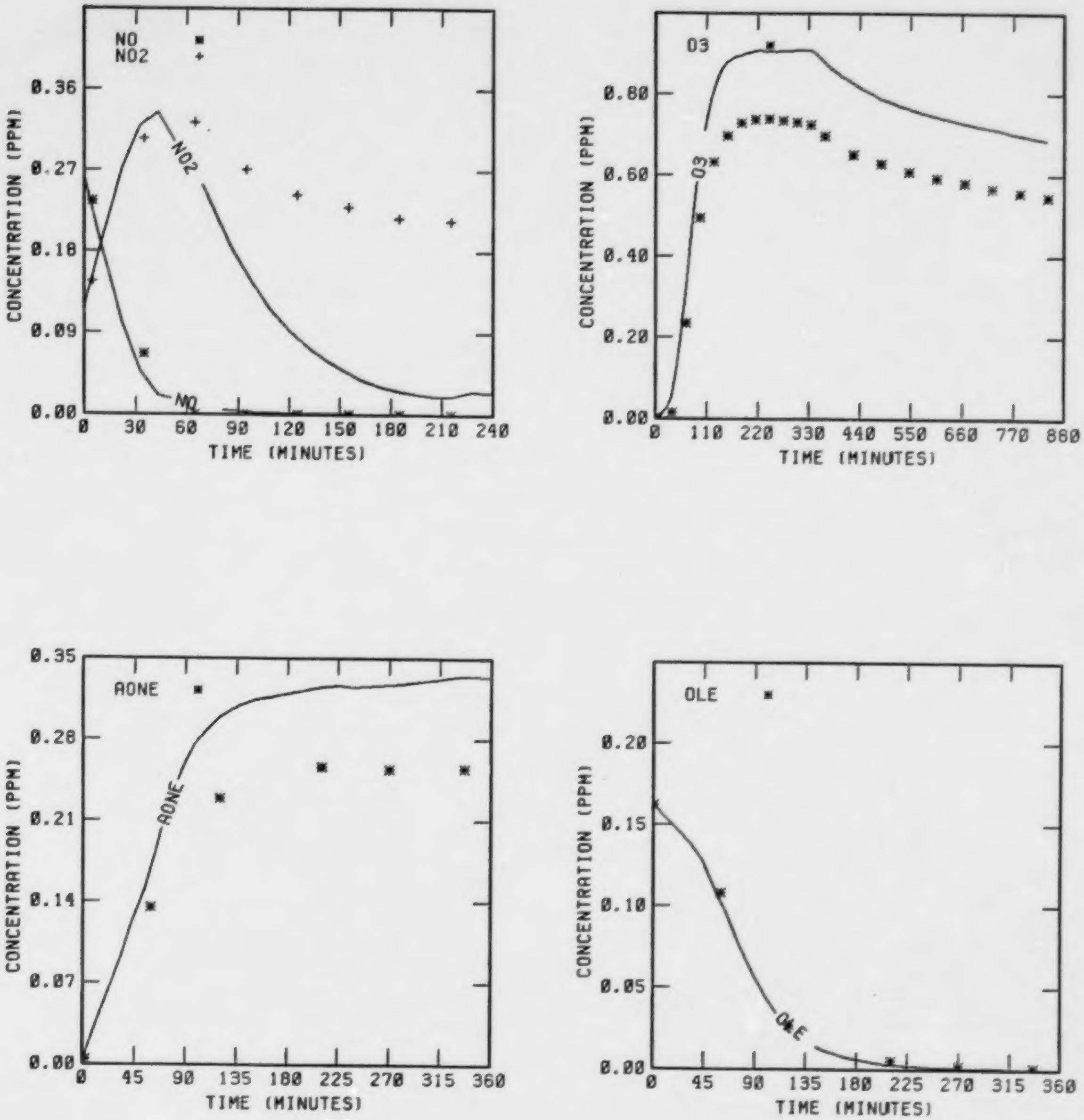


FIGURE C-8. SIMULATION RESULTS FOR OTCR.72783

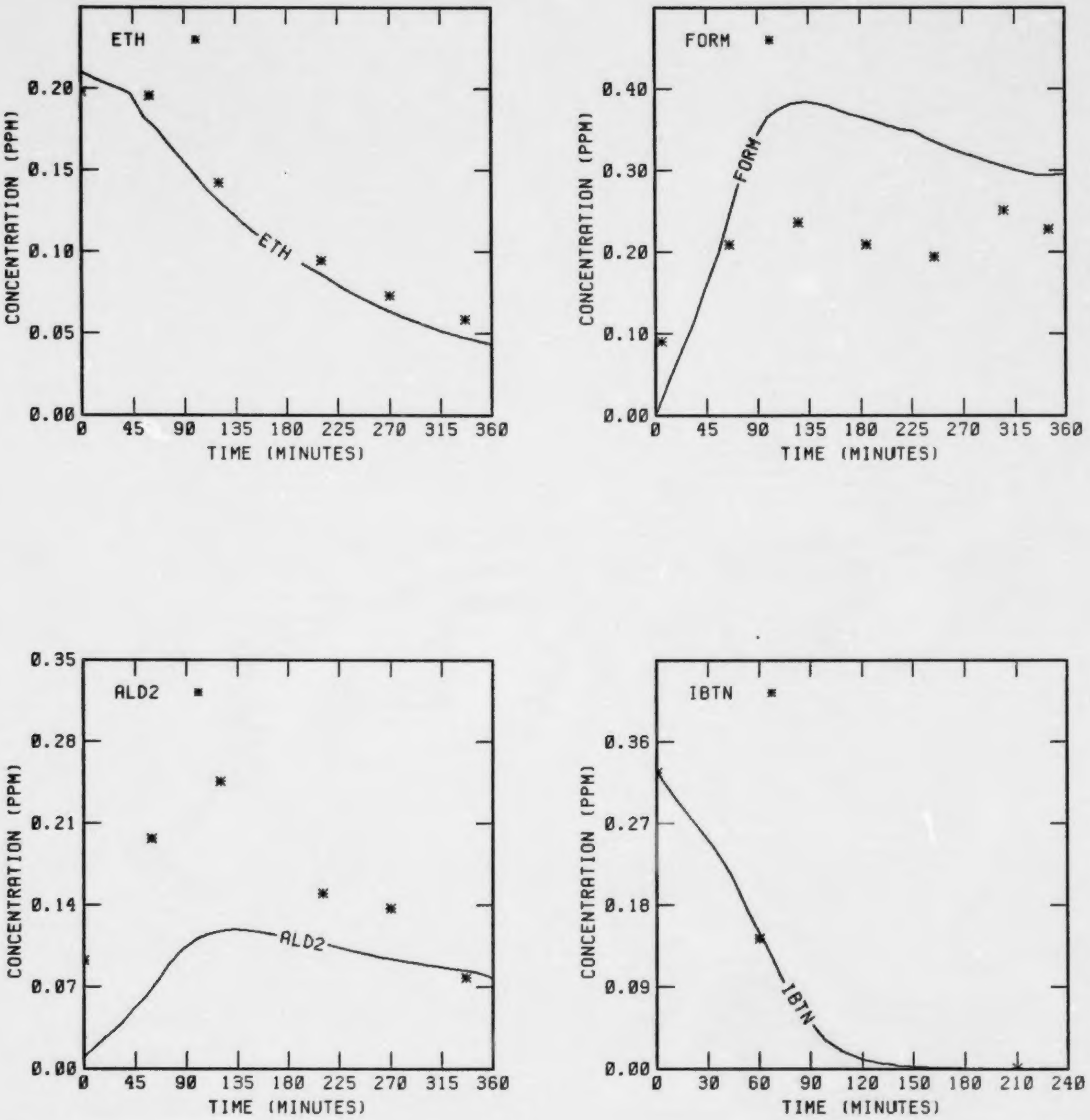


FIGURE C-8. SIMULATION RESULTS FOR OTCR.72783

(continued).

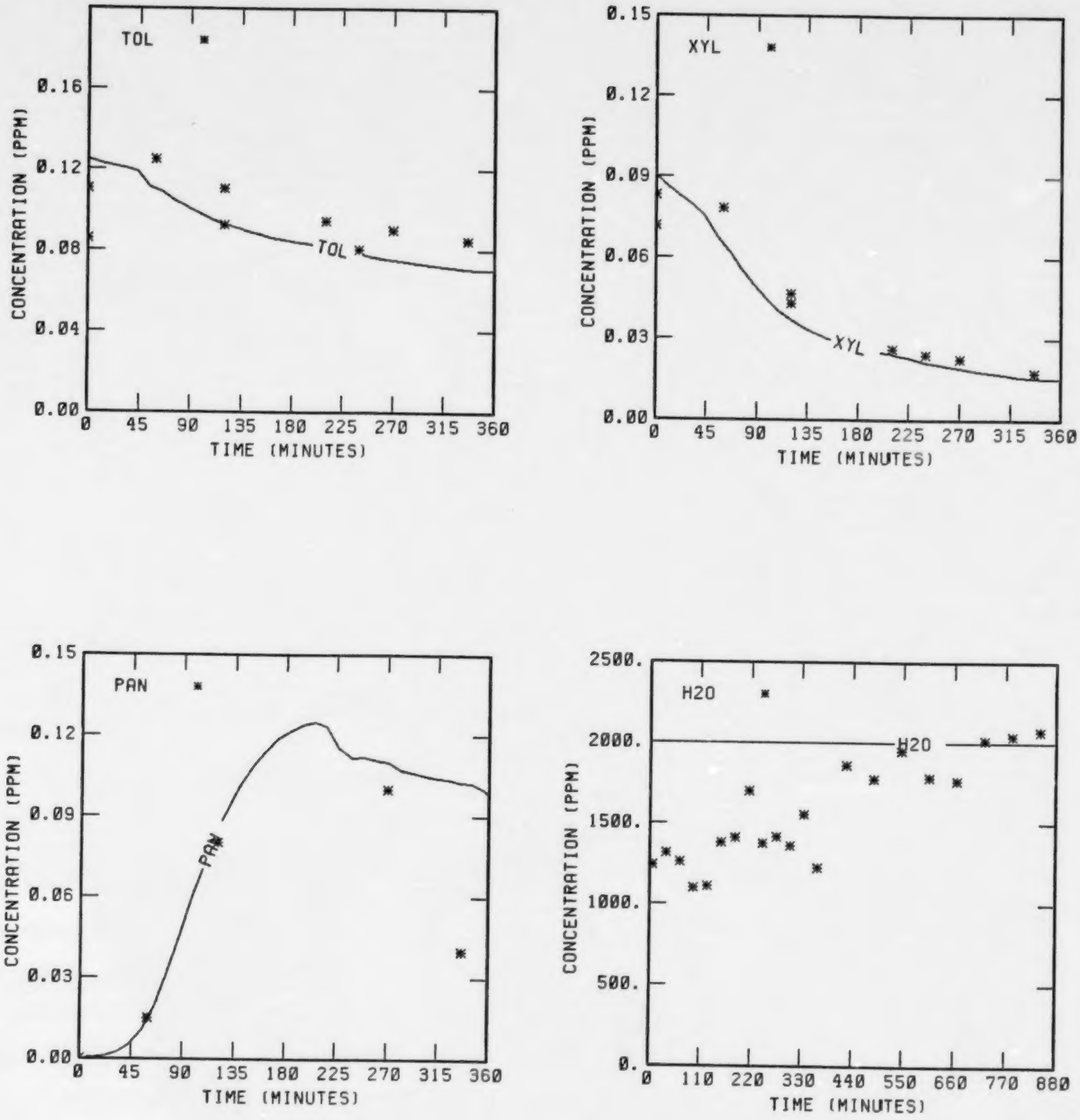


FIGURE C-8. SIMULATION RESULTS FOR OTCR.72783

(continued).

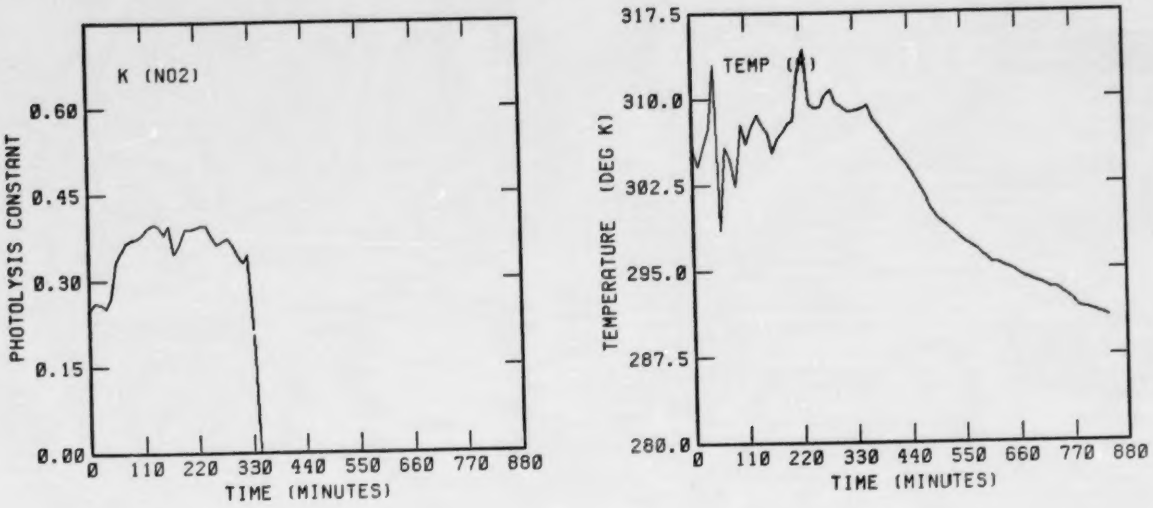


FIGURE C-8. SIMULATION RESULTS FOR
OTCR.72783

(concluded).

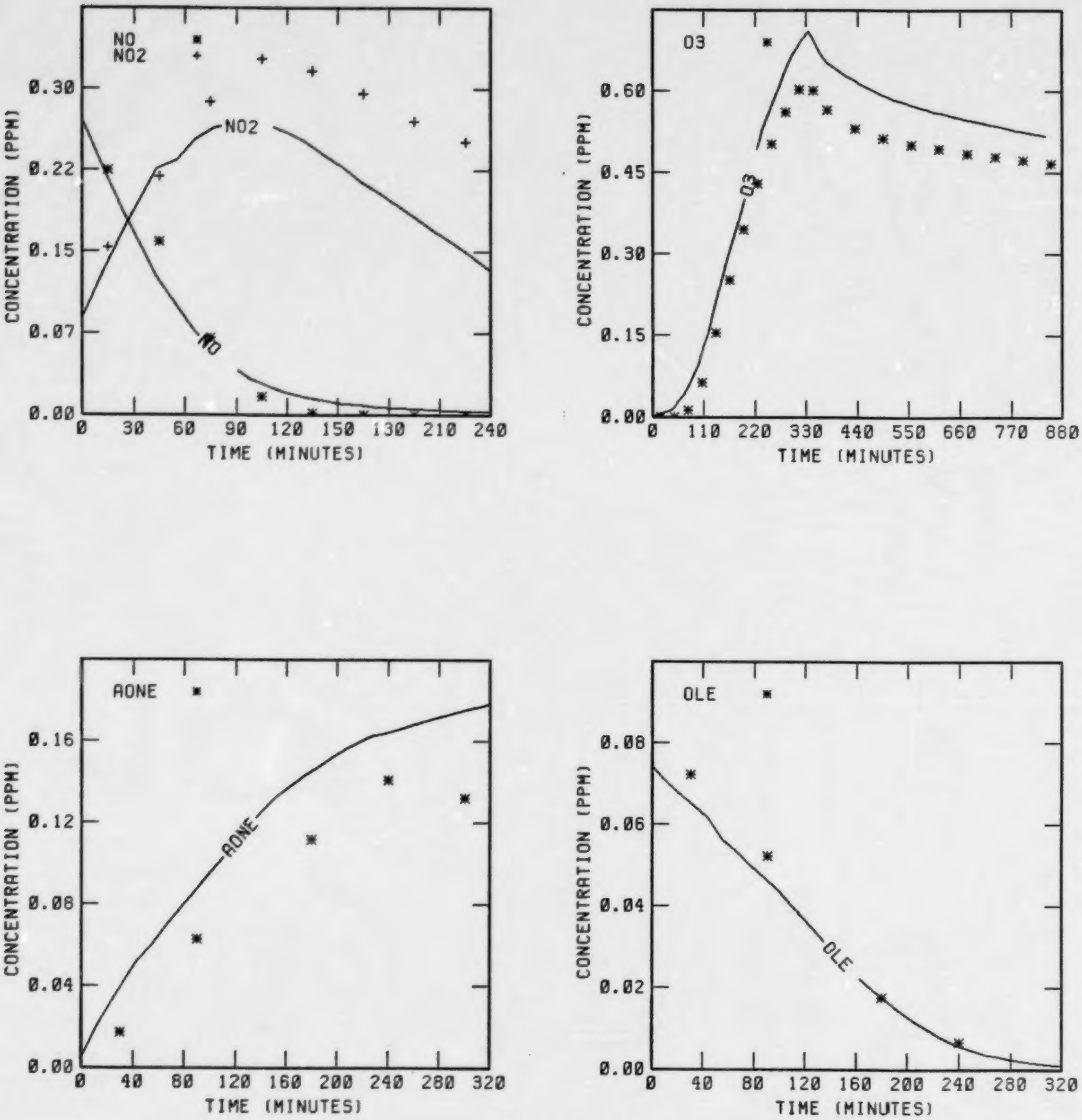


FIGURE C-9. SIMULATION RESULTS FOR
OTCB.72783

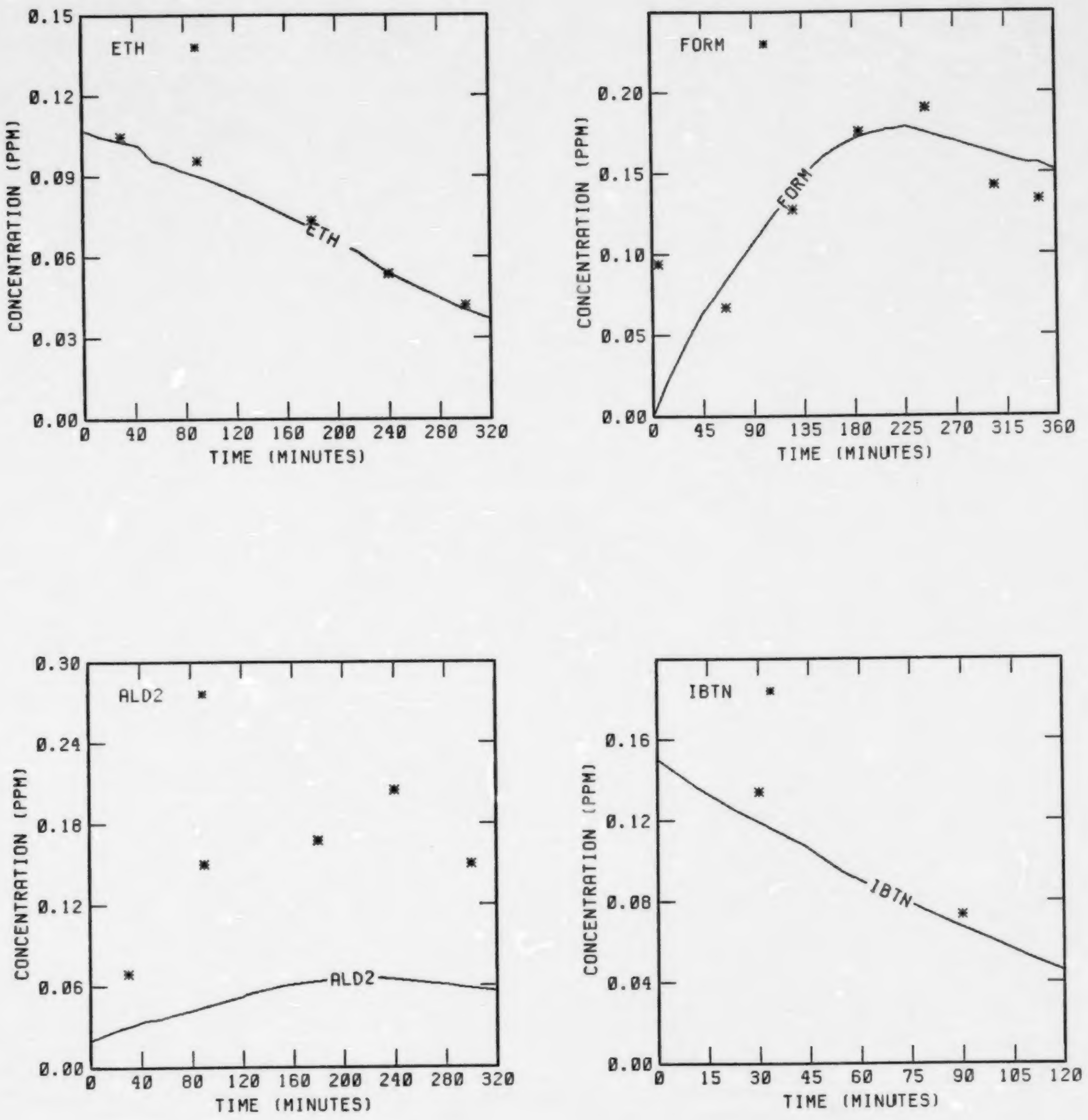


FIGURE C-9. SIMULATION RESULTS FOR OTCB.72783

(continued)

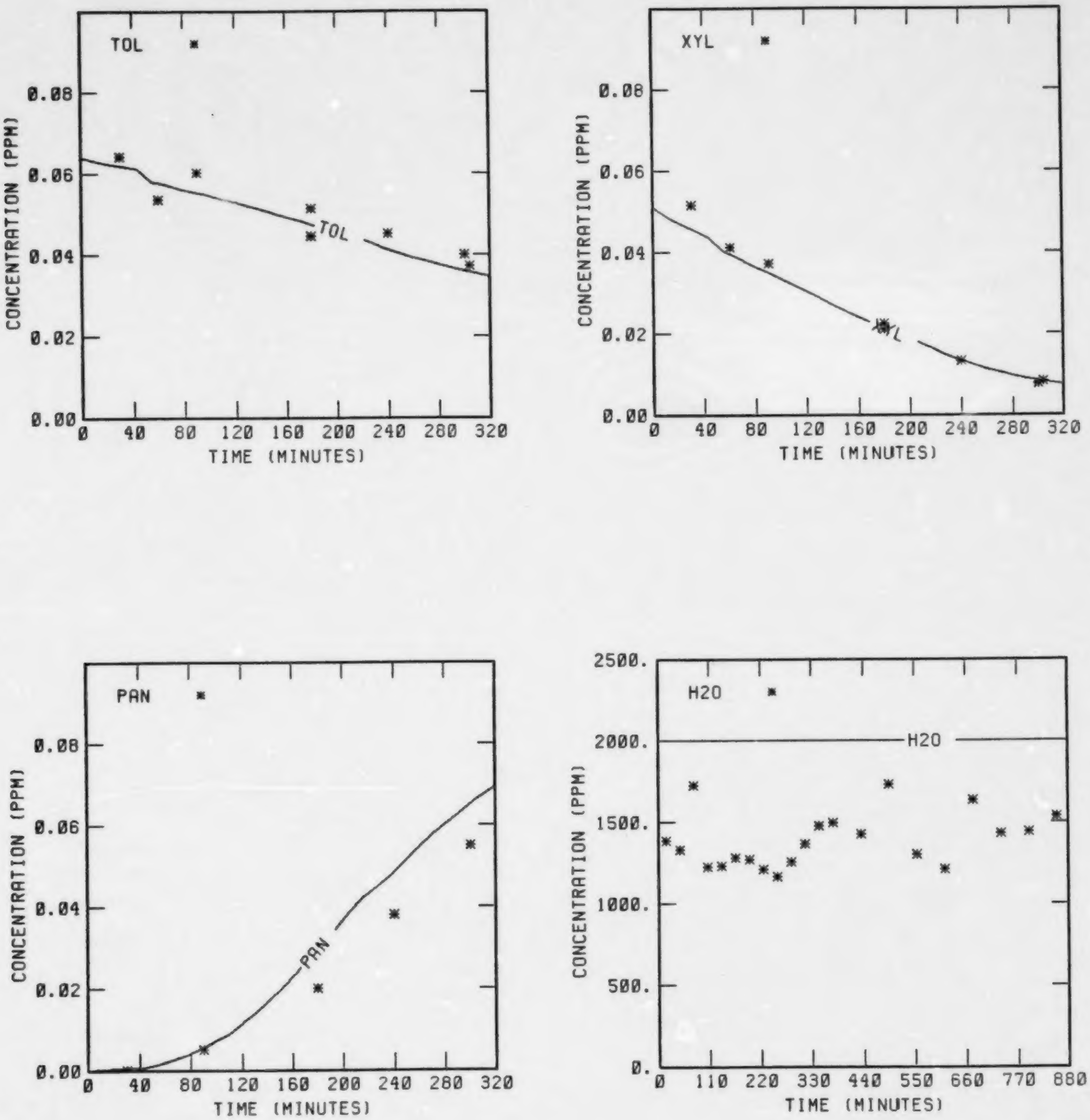


FIGURE C-9. SIMULATION RESULTS FOR OTCB.72783

(continued).

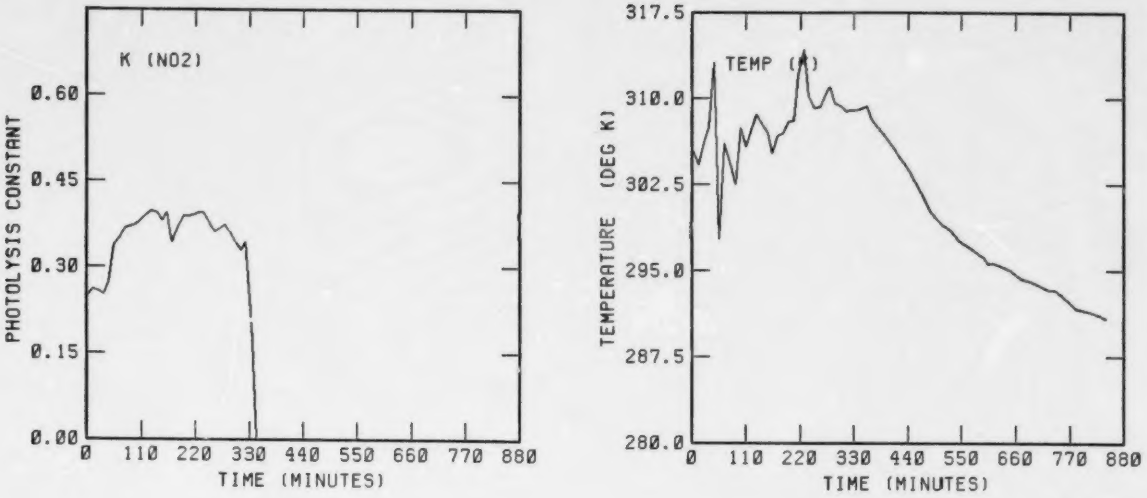


FIGURE C-9. SIMULATION RESULTS FOR
OTCB.72783

(concluded).

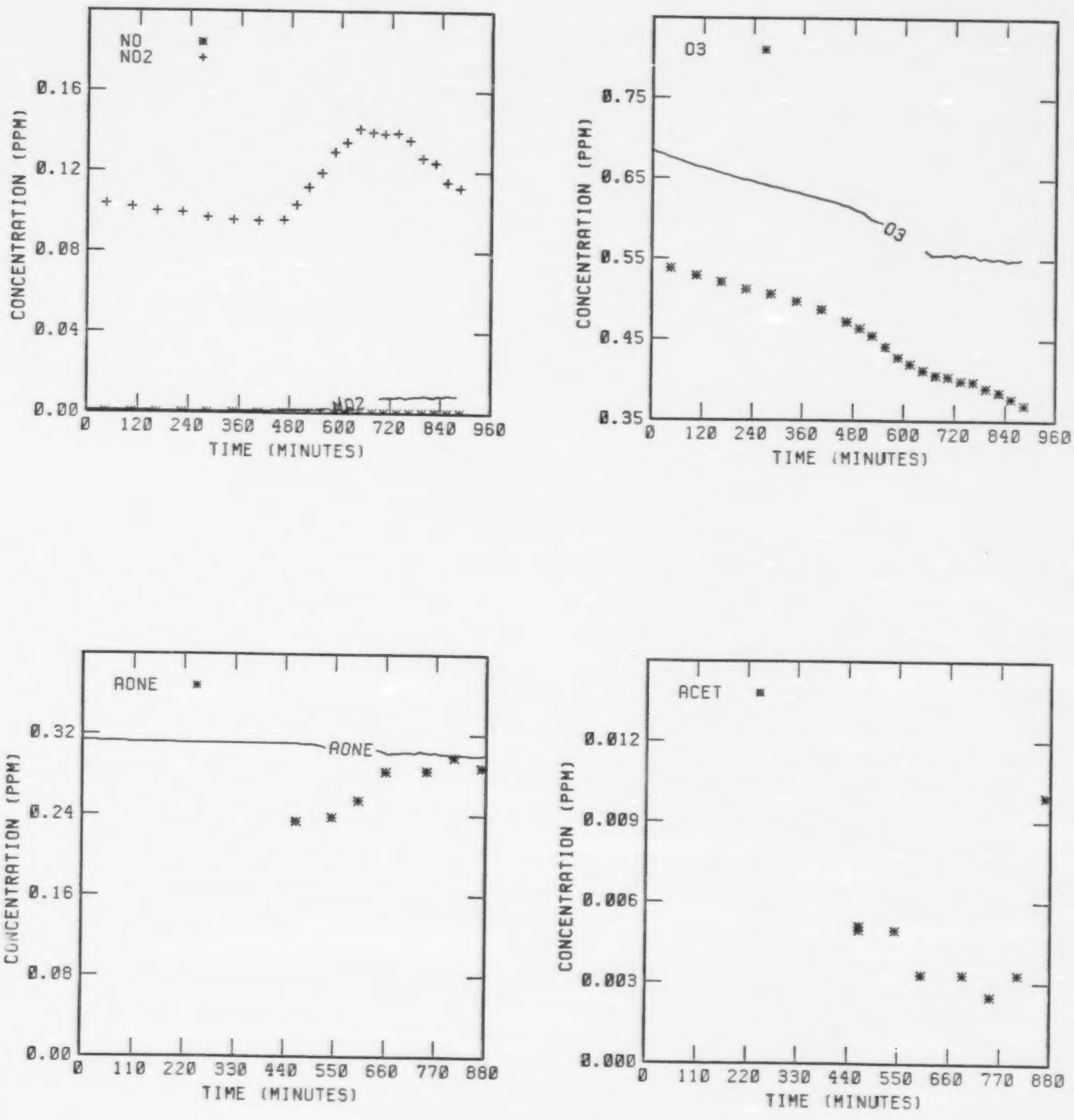


FIGURE C-10. SIMULATION RESULTS FOR
OTCR.72883

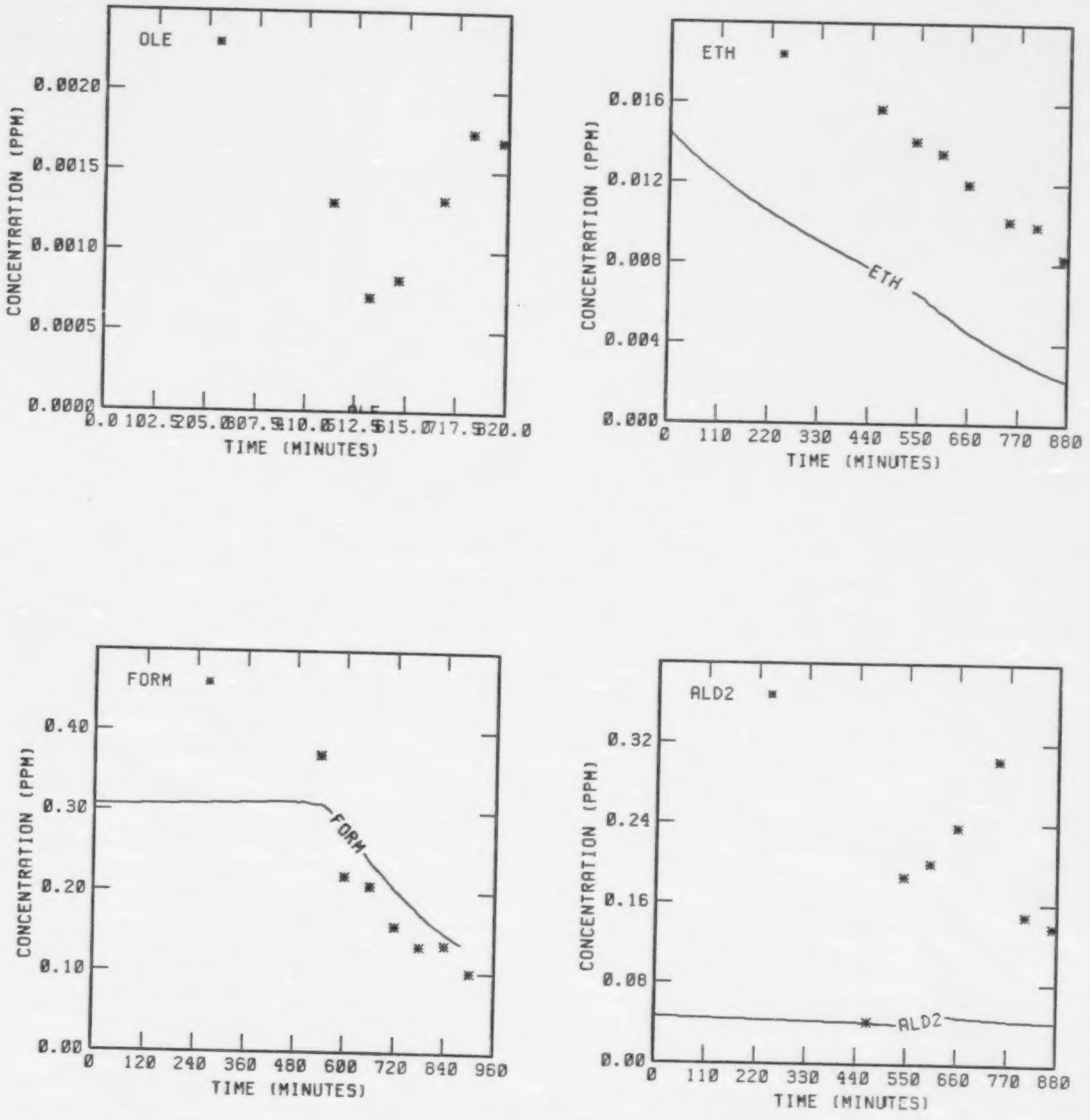


FIGURE C-10. SIMULATION RESULTS FOR
OTCR.72883
(continued).

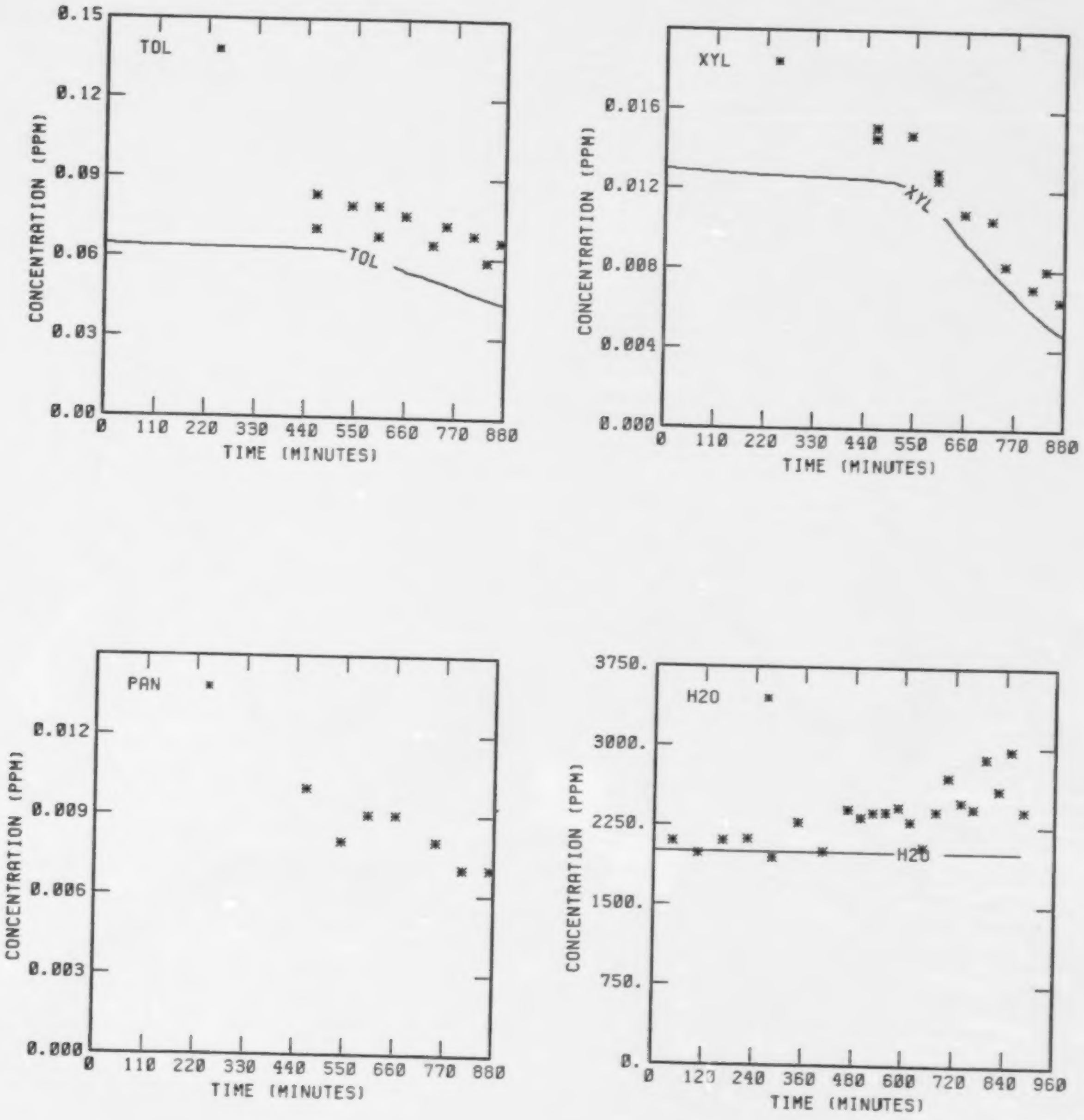


FIGURE C-10. SIMULATION RESULTS FOR OTCR.72883

(continued).

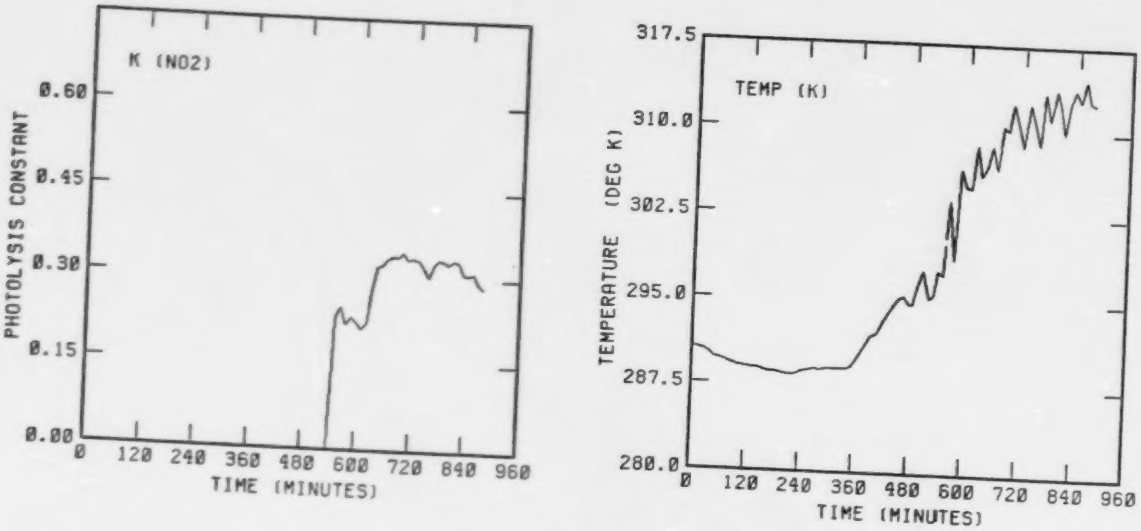


FIGURE C-10. SIMULATION RESULTS FOR
OTCR.72883

(concluded).

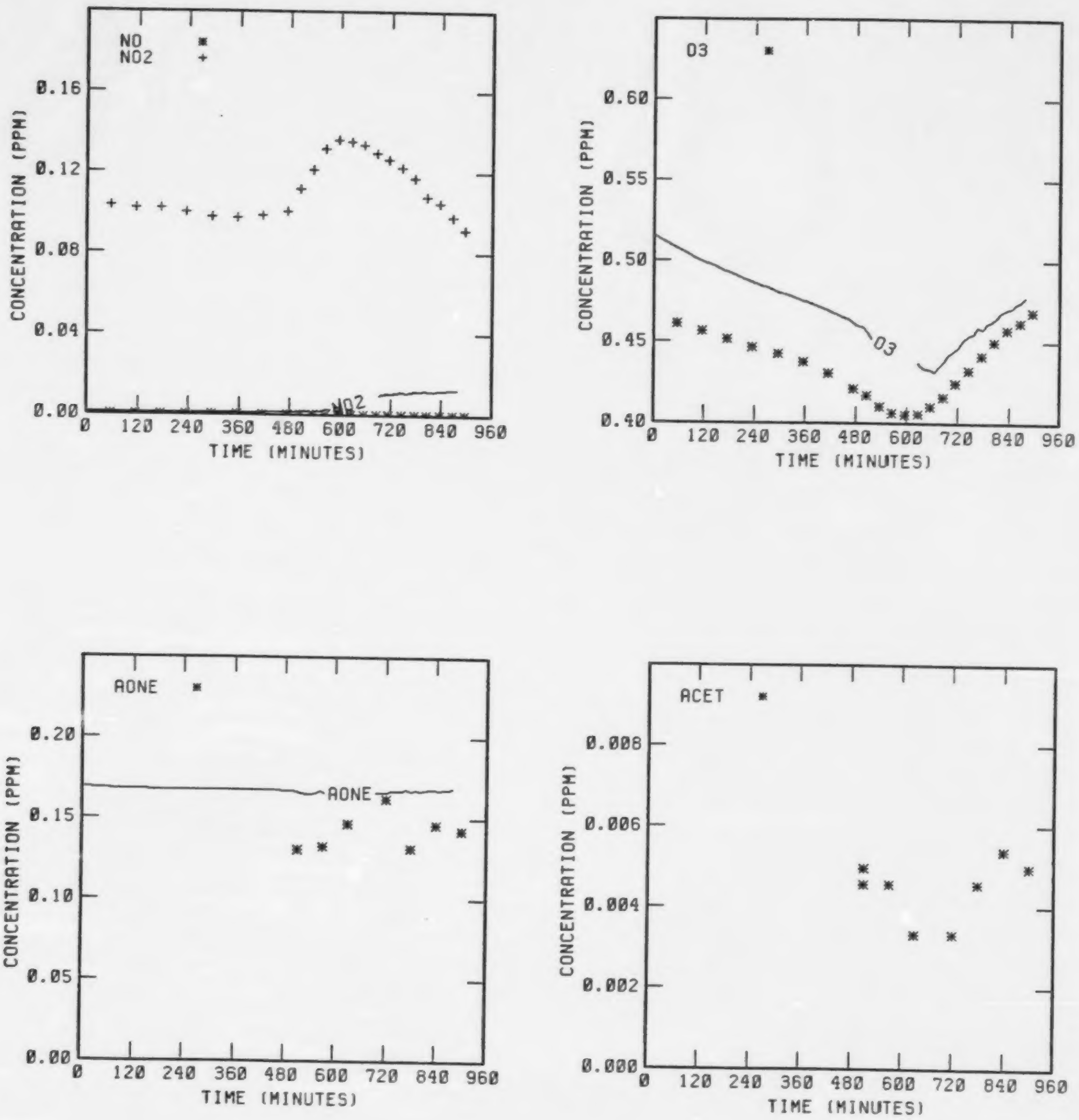


FIGURE **C-11.** SIMULATION RESULTS FOR
OTCB.72883

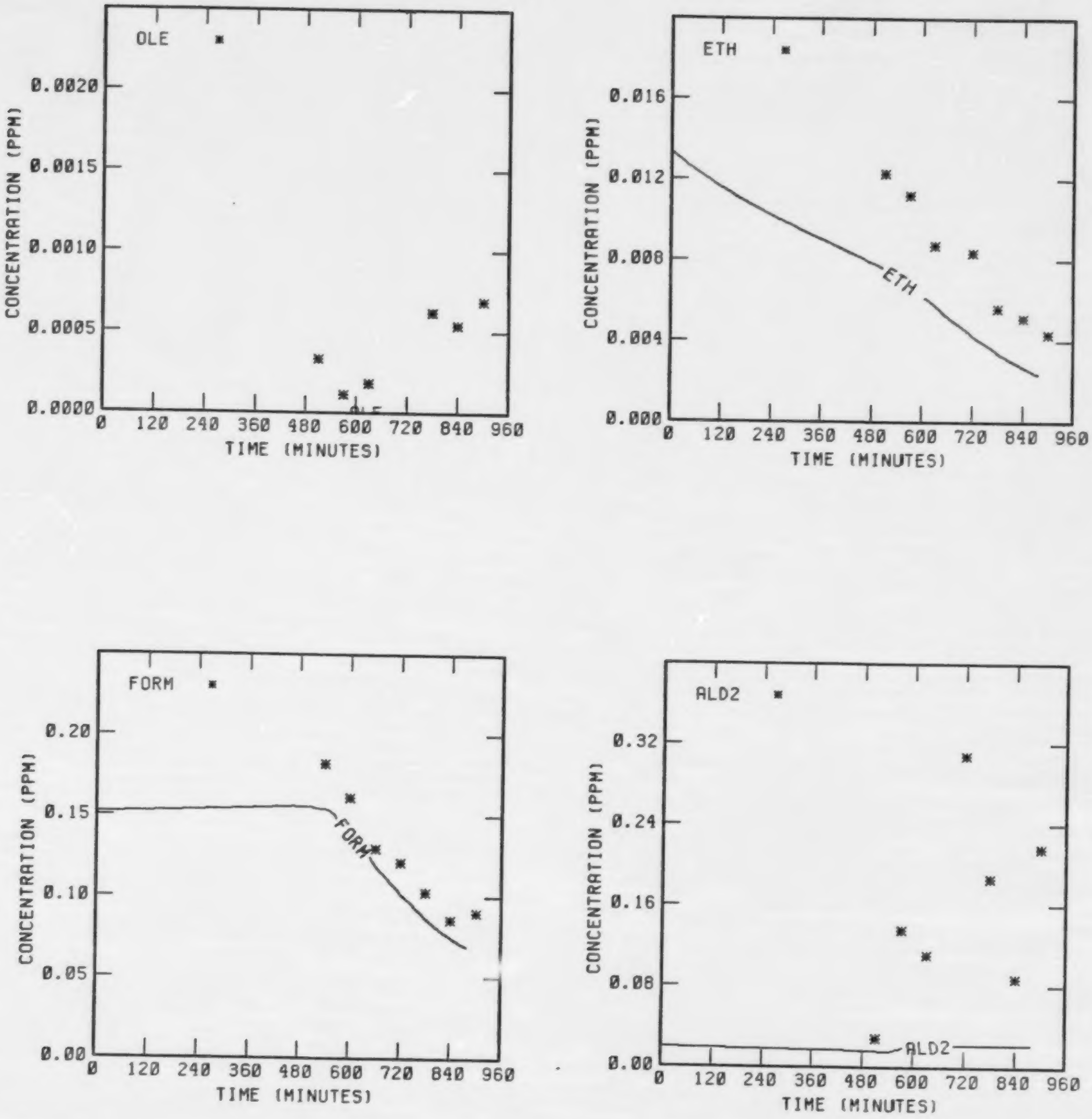
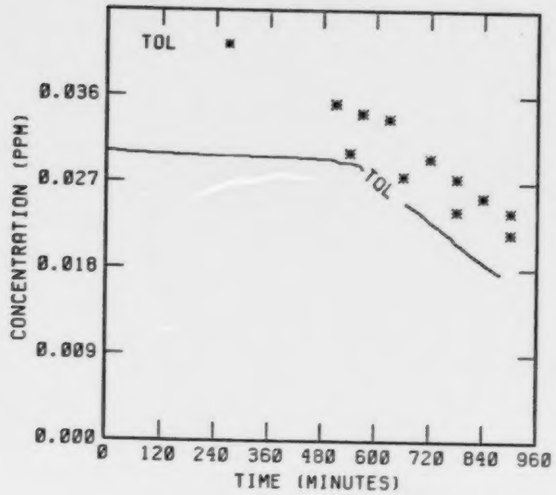


FIGURE C-11. SIMULATION RESULTS FOR
OTCB.72883

(continued).



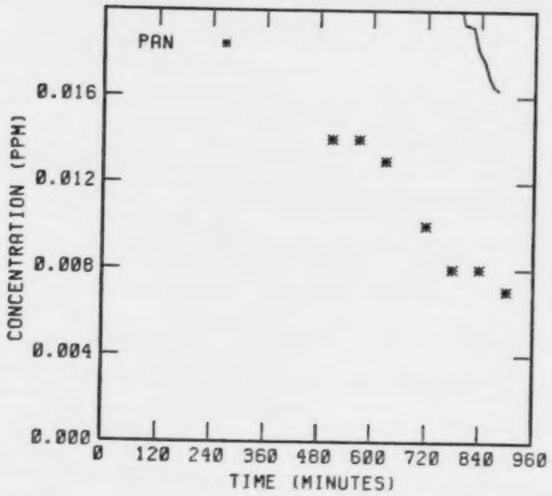


FIGURE C-11. SIMULATION RESULTS FOR OTCB.72883

(concluded).

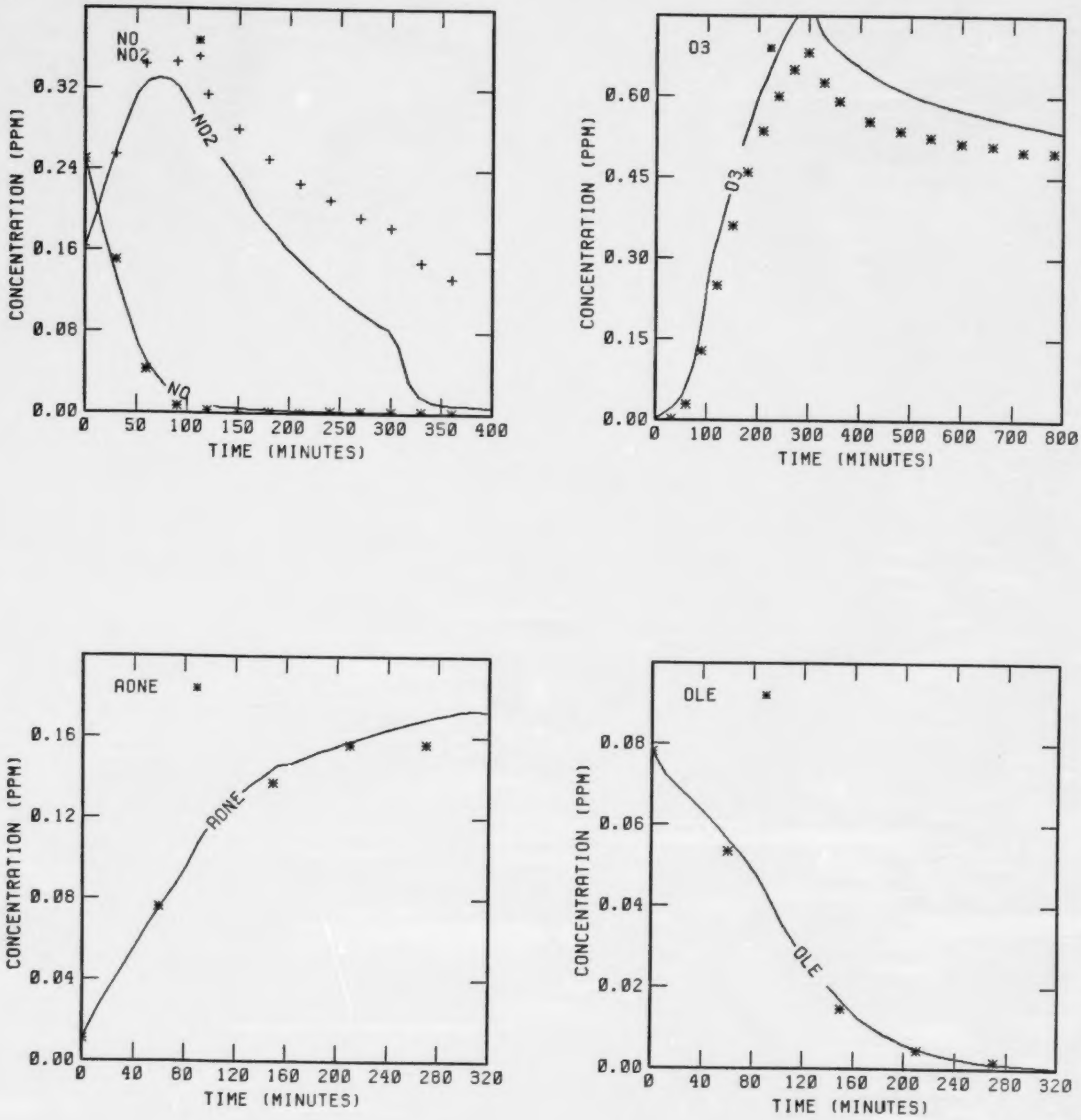


FIGURE C-12. SIMULATION RESULTS FOR
OTCB.80283

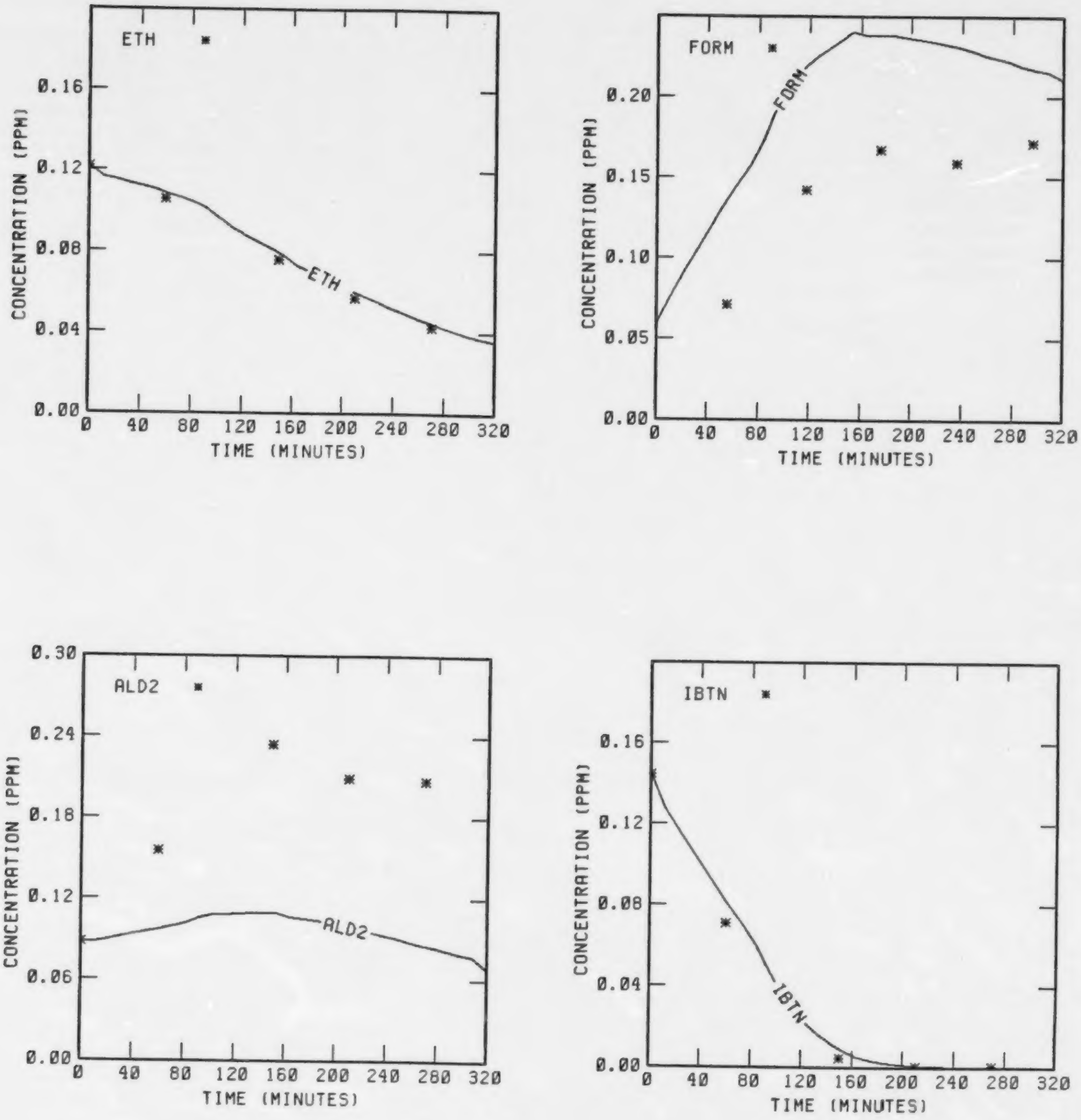


FIGURE C-12. SIMULATION RESULTS FOR
OTCB.80283
(continued).

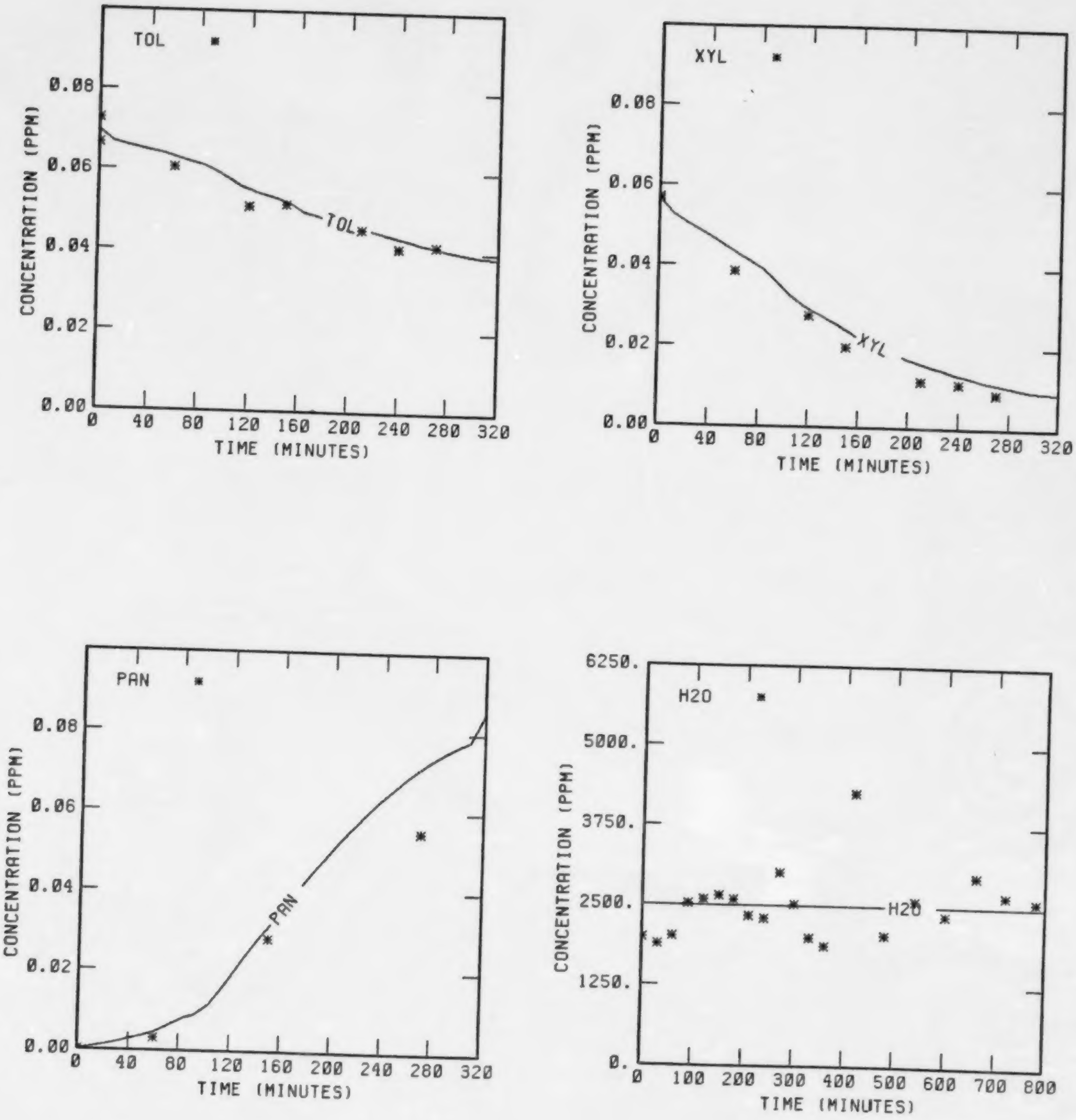


FIGURE C-12. SIMULATION RESULTS FOR OTCB.80283 (continued).

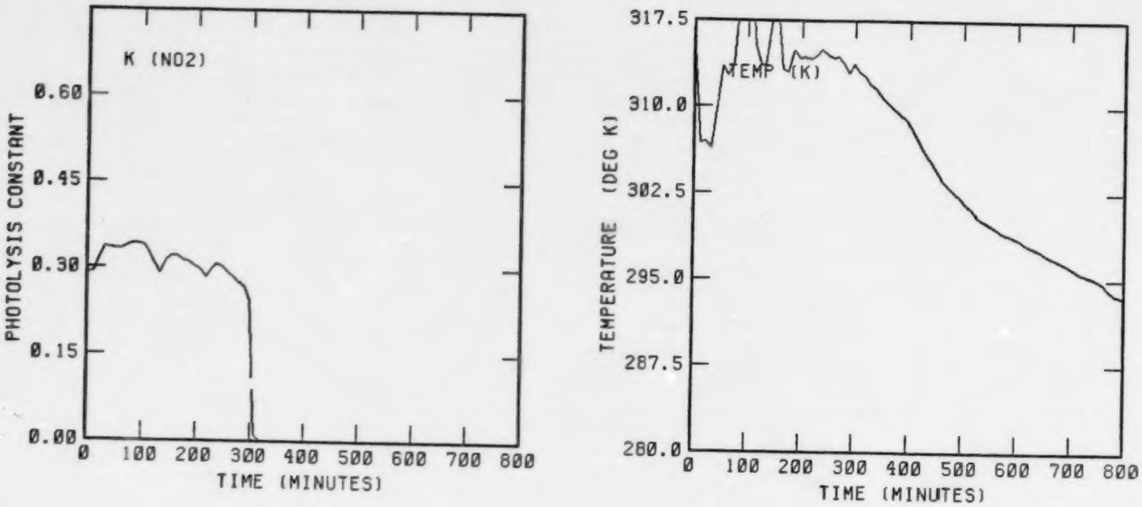


FIGURE C-12. SIMULATION RESULTS FOR
OTCB.80283

(concluded).

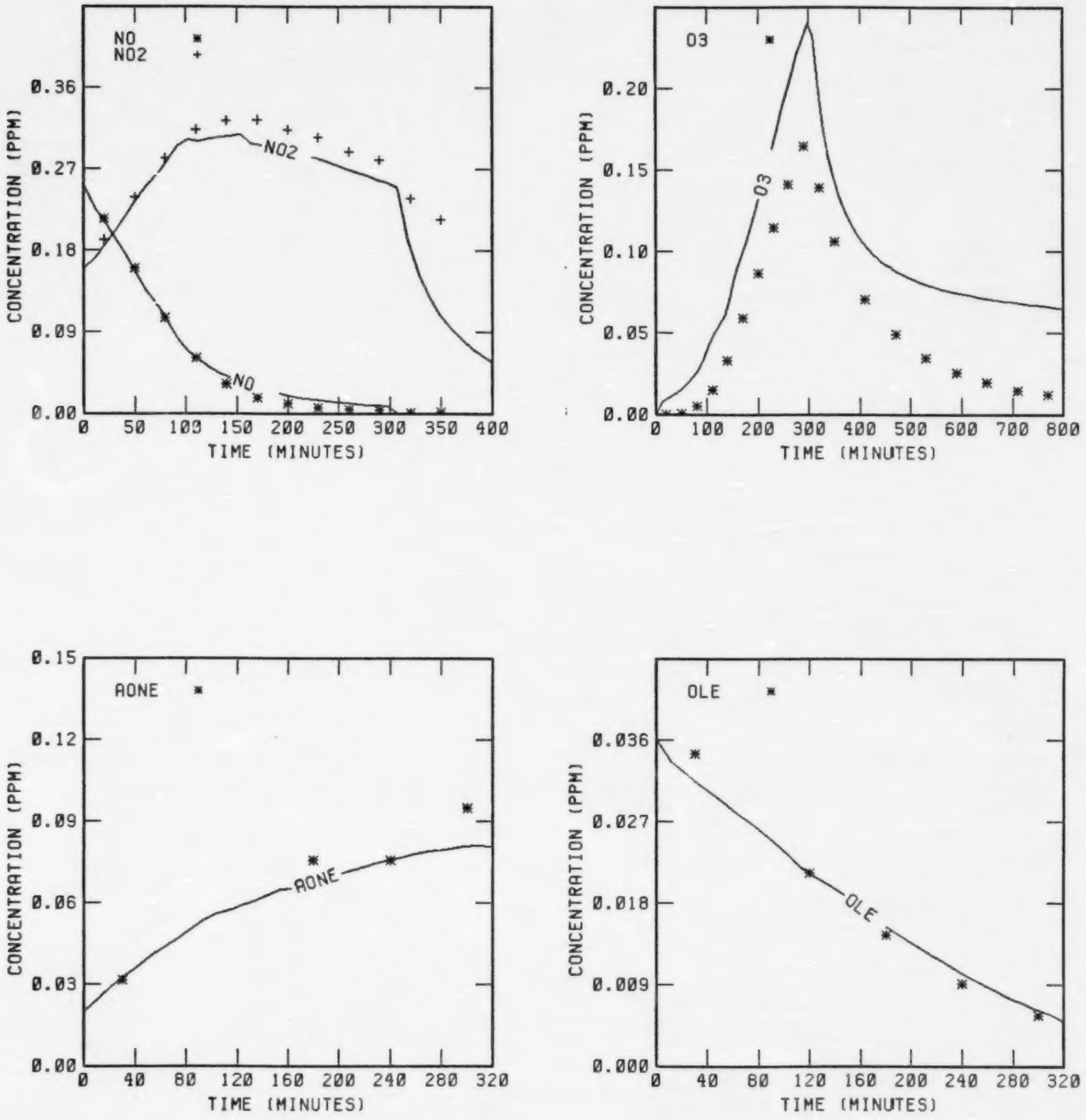


FIGURE C-13. SIMULATION RESULTS FOR
OTCR.80283

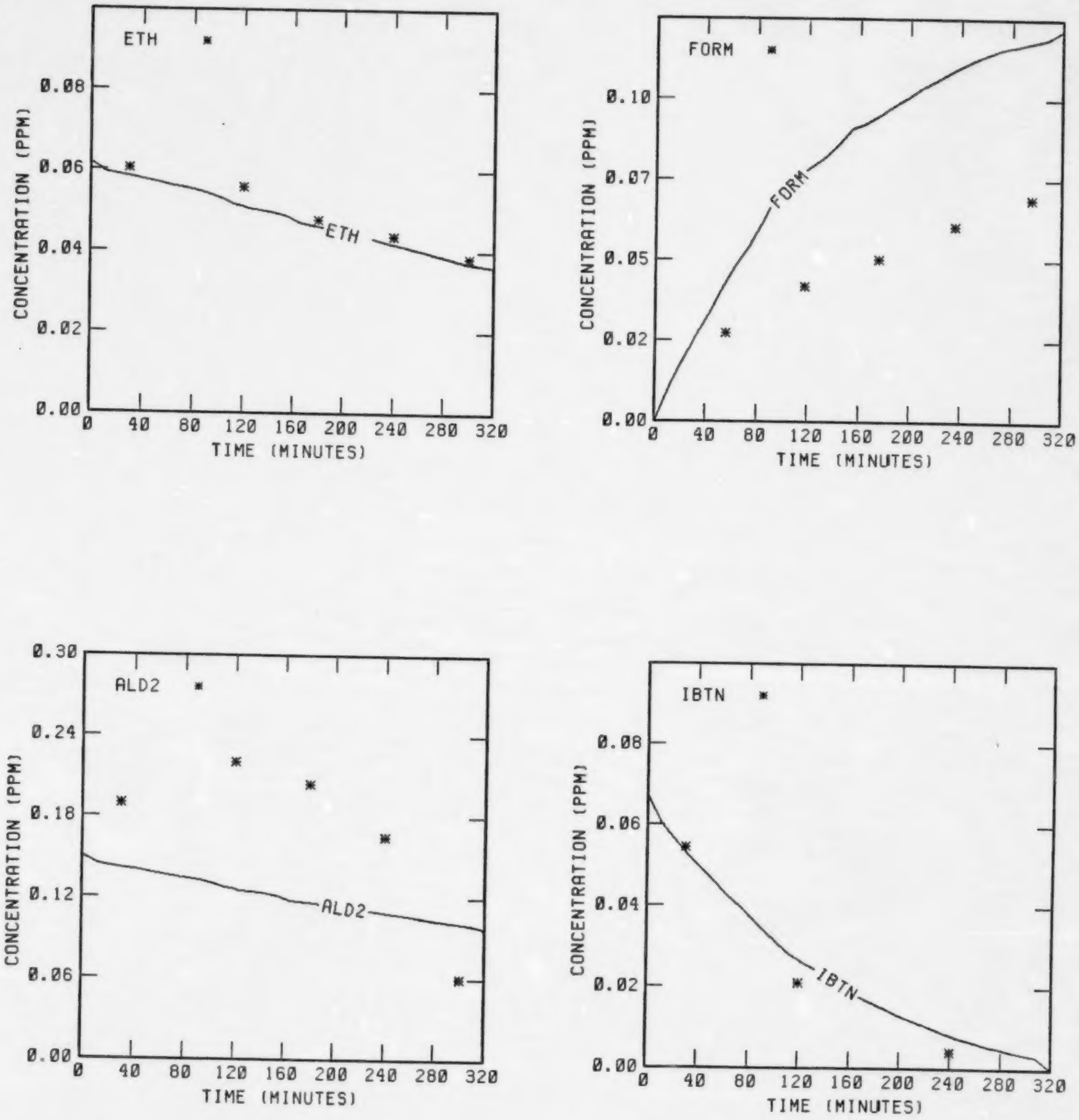


FIGURE C-13. SIMULATION RESULTS FOR
OTCR.80283
(continued).

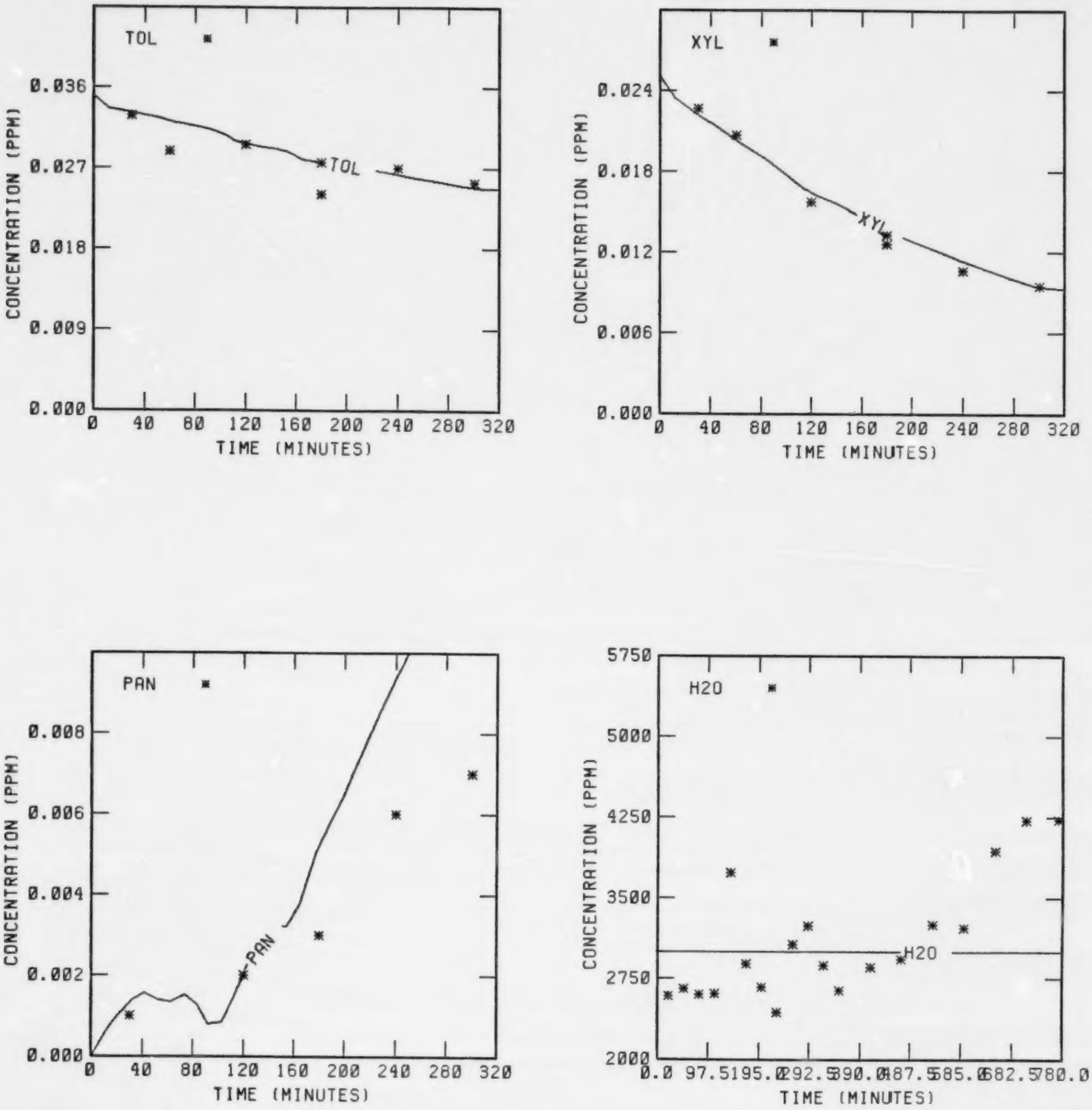


FIGURE C-13. SIMULATION RESULTS FOR OTCR.80283

(continued).

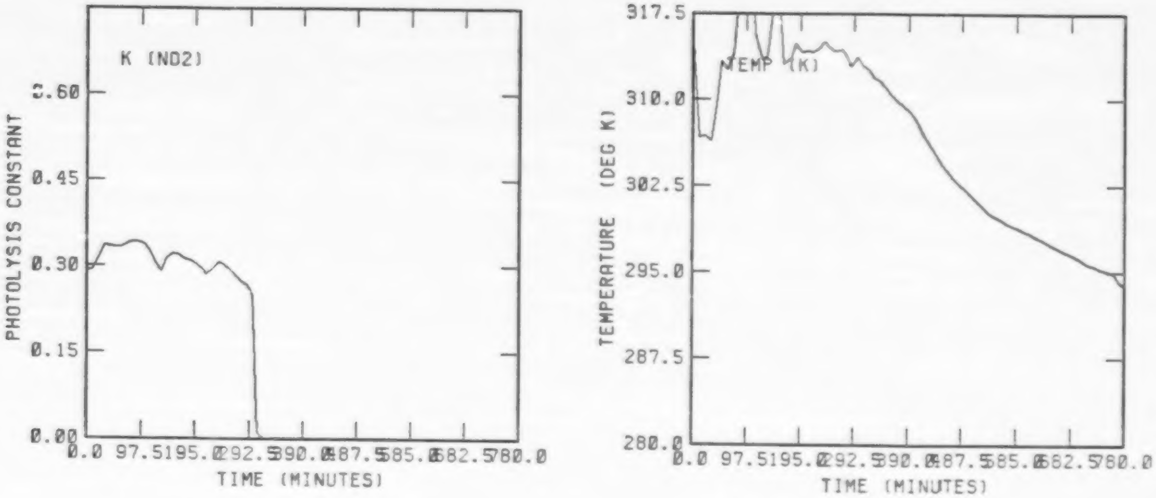


FIGURE C-13. SIMULATION RESULTS FOR
DTCR.80283
(concluded).

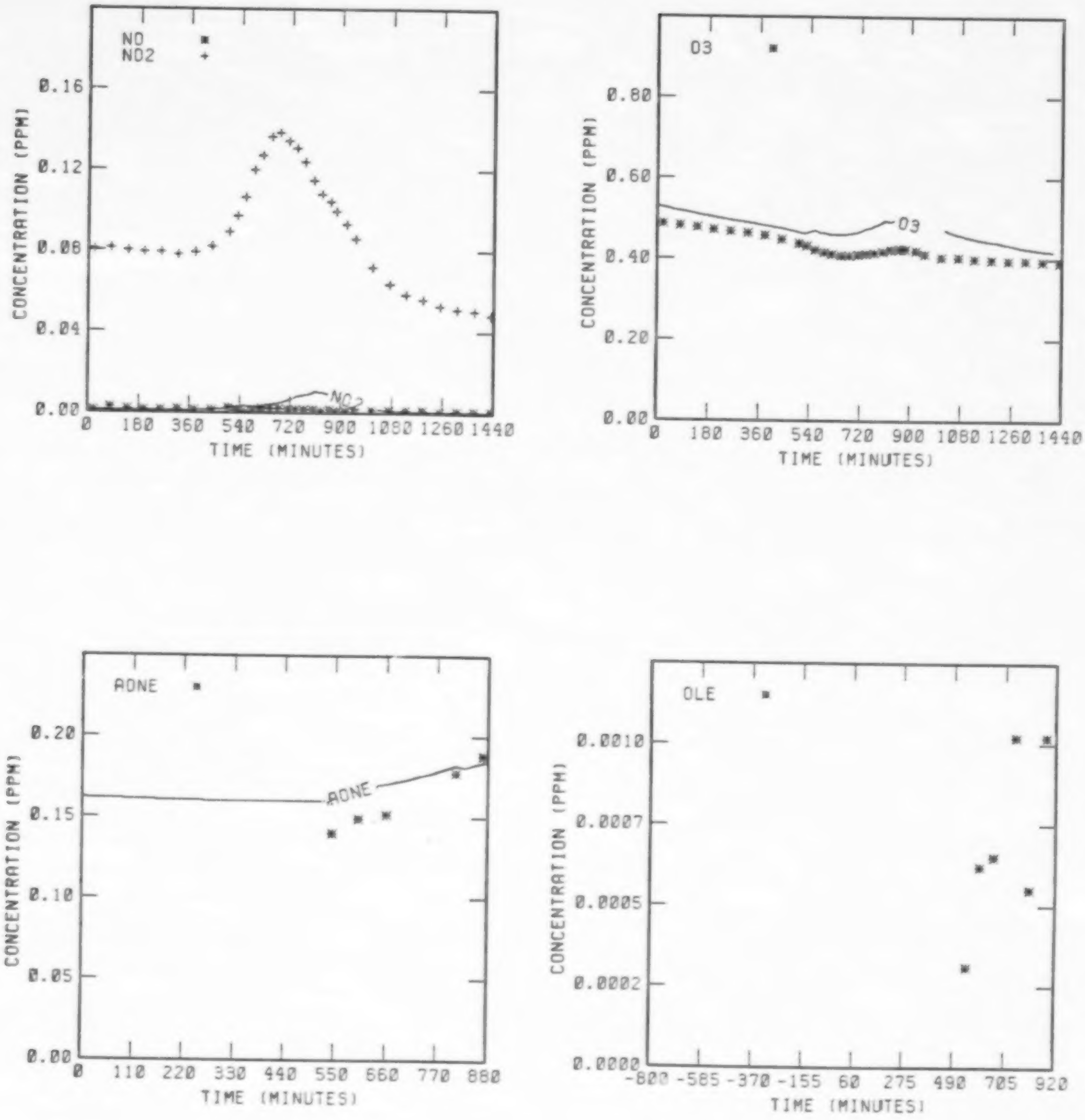


FIGURE C-14. SIMULATION RESULTS FOR
OTCB.80383

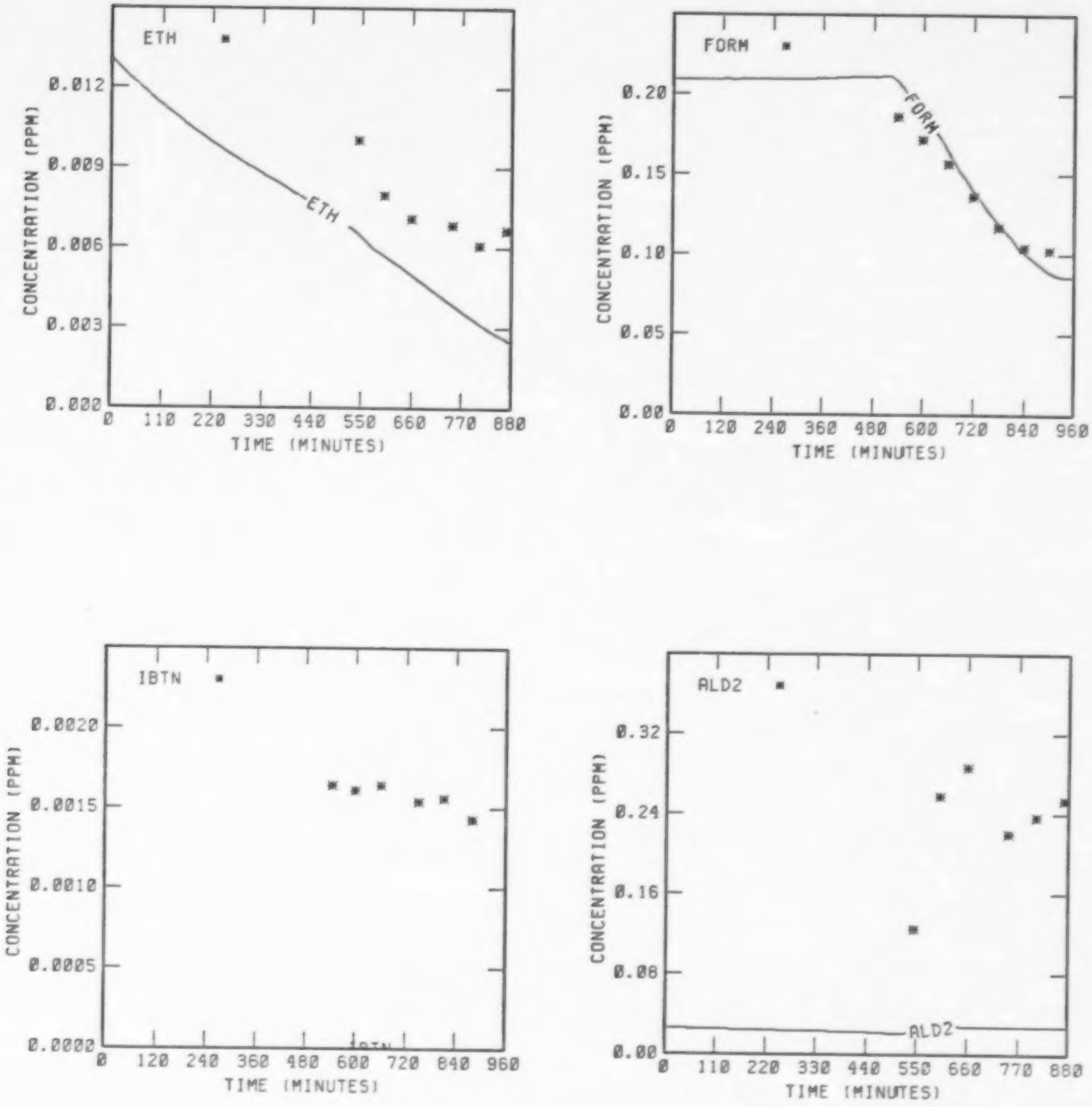


FIGURE C-14. SIMULATION RESULTS FOR
OTCB.80383

(continued).

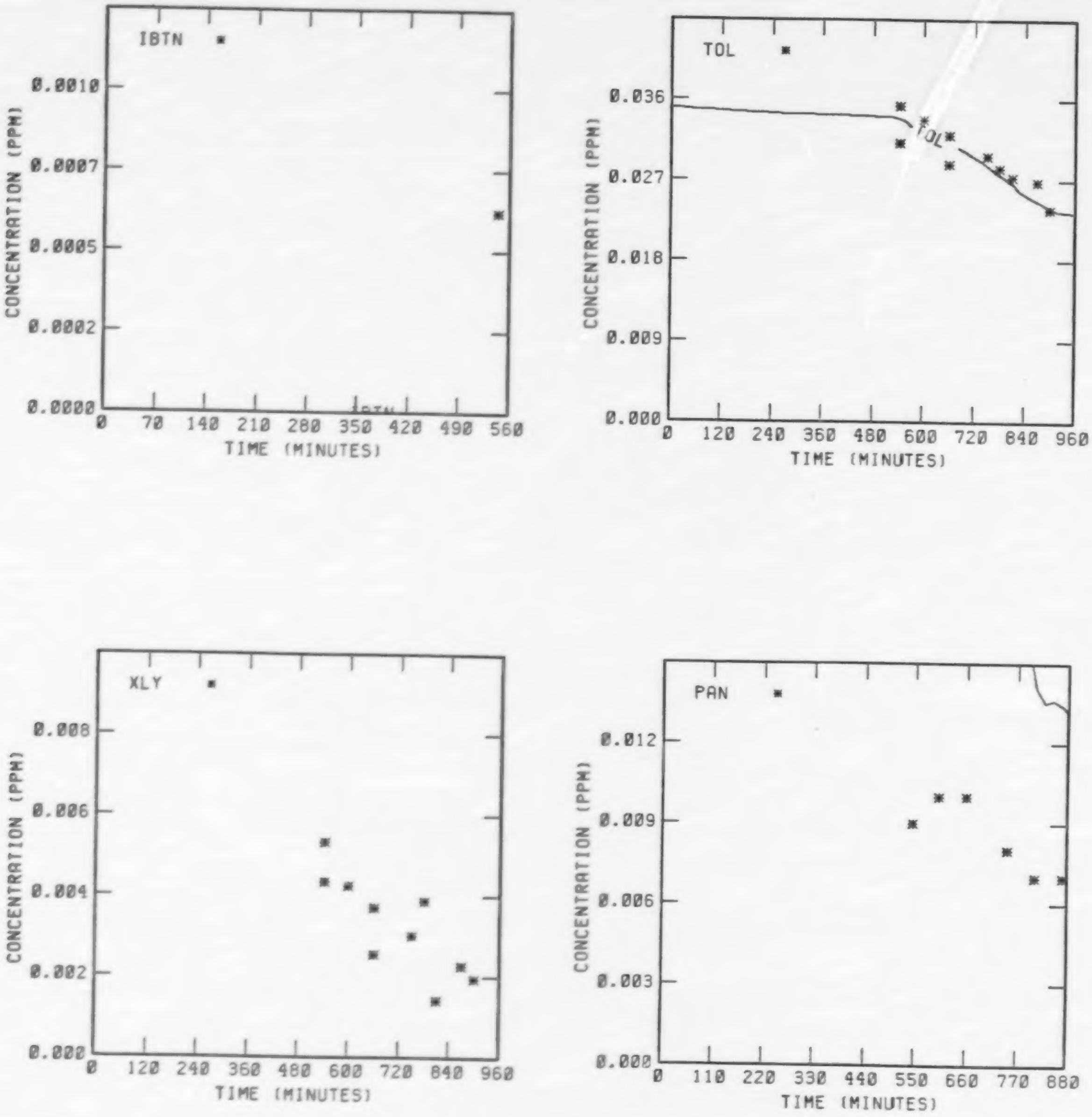


FIGURE C-14. SIMULATION RESULTS FOR
OTCB.80383

(continued).

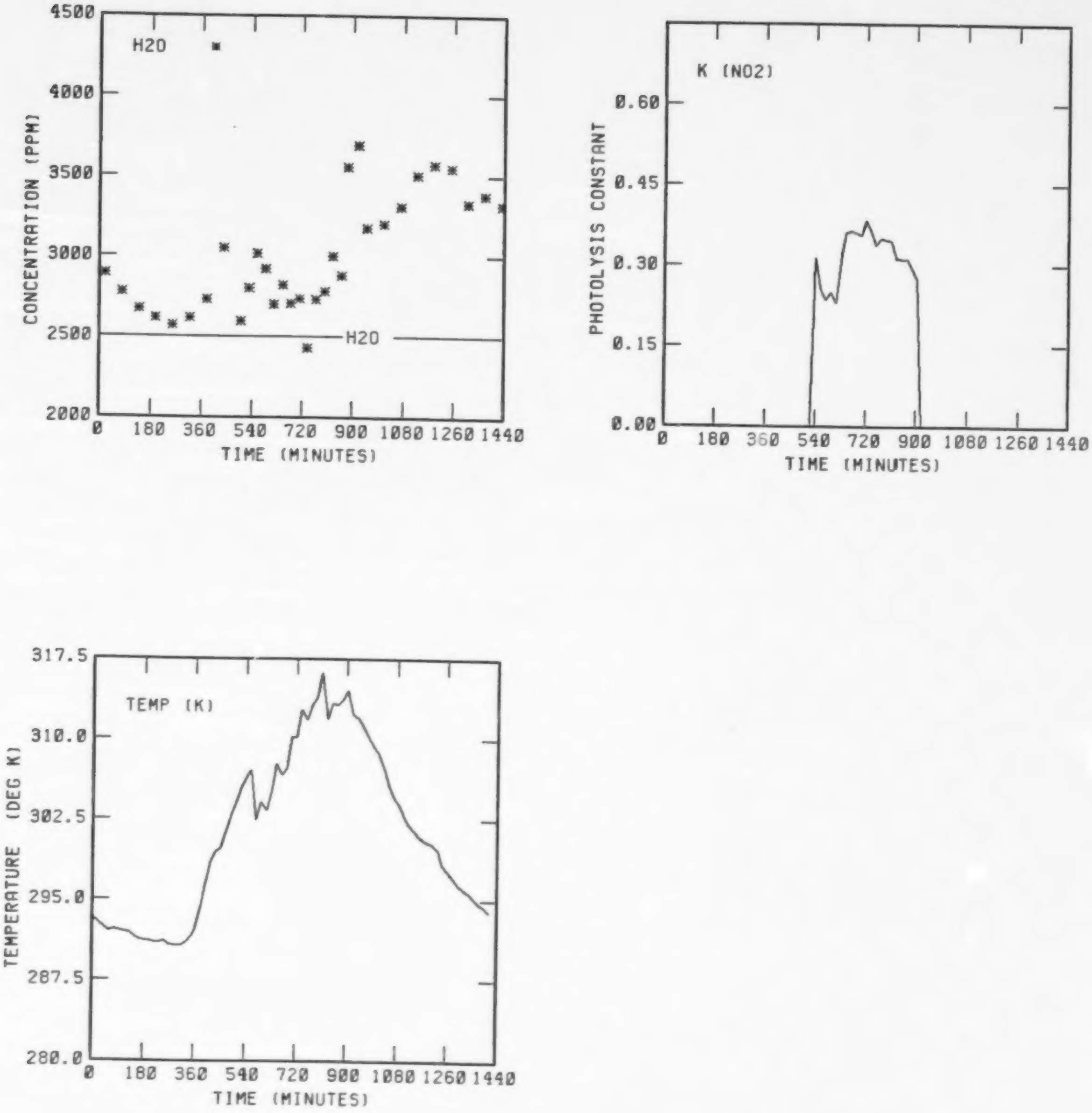


FIGURE **C-14.** SIMULATION RESULTS FOR
OTCB.80383
(concluded).

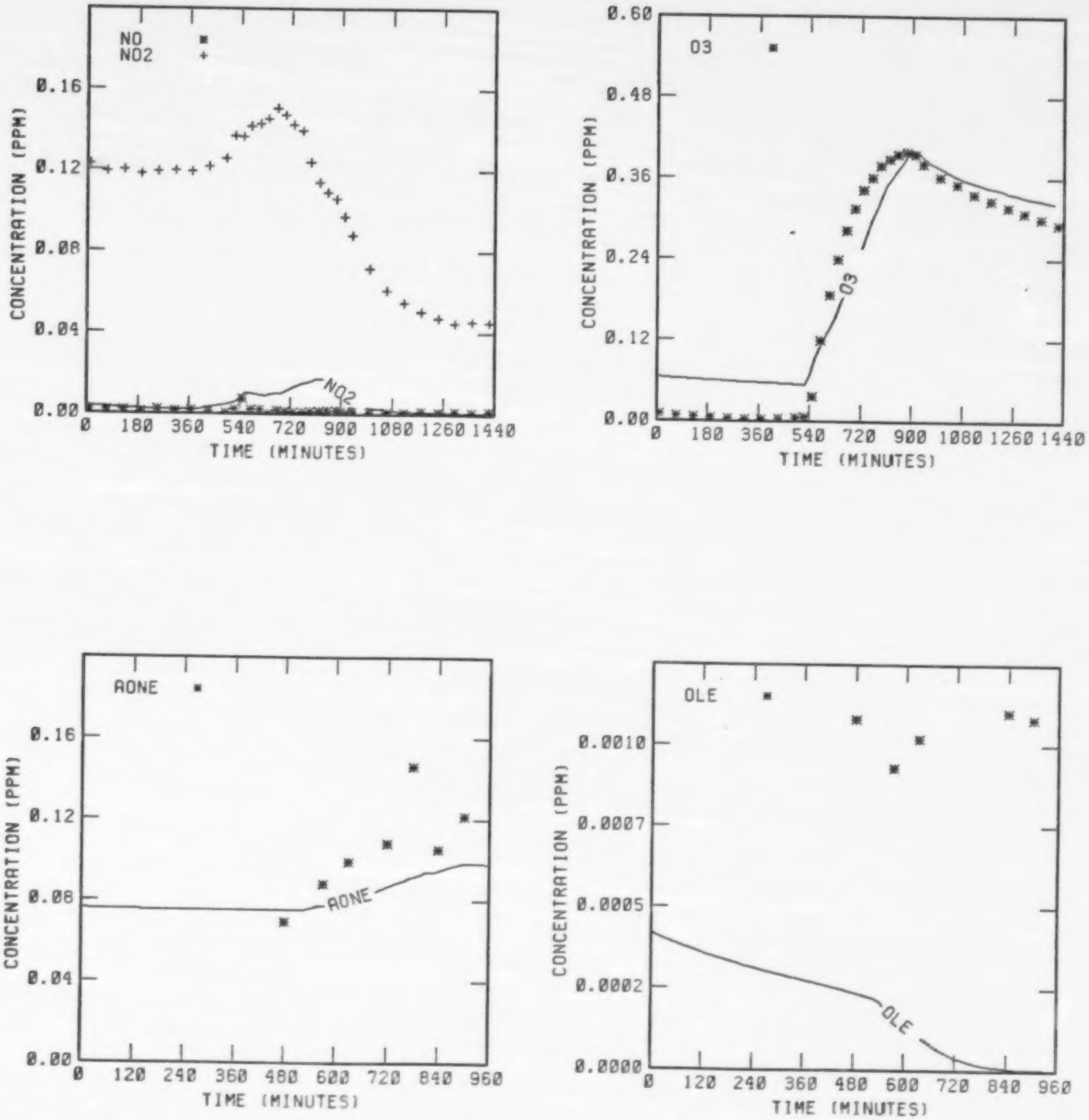


FIGURE C-15. SIMULATION RESULTS FOR
OTCR.80383

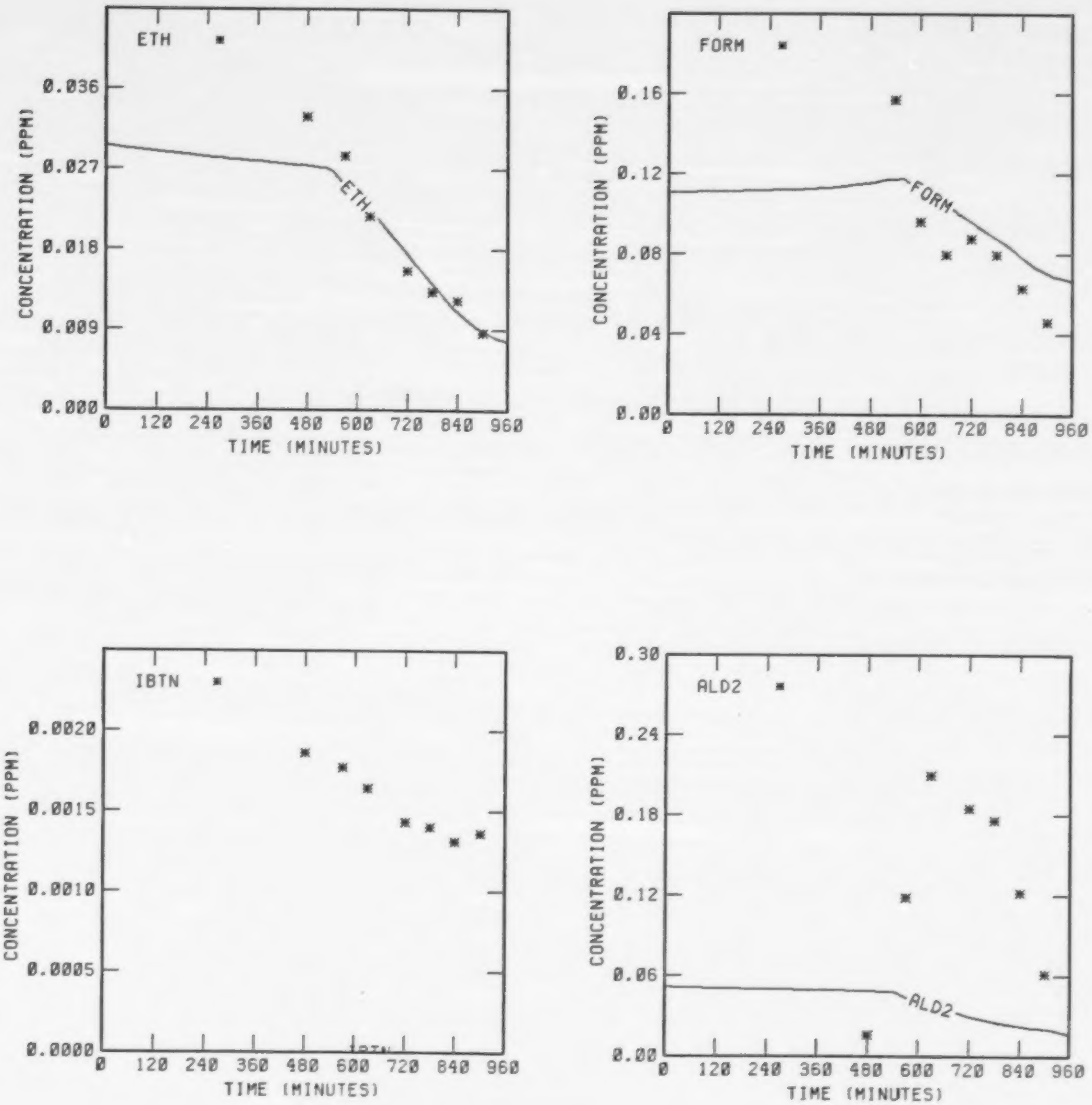


FIGURE C-15. SIMULATION RESULTS FOR
OTCR.80383
(continued).

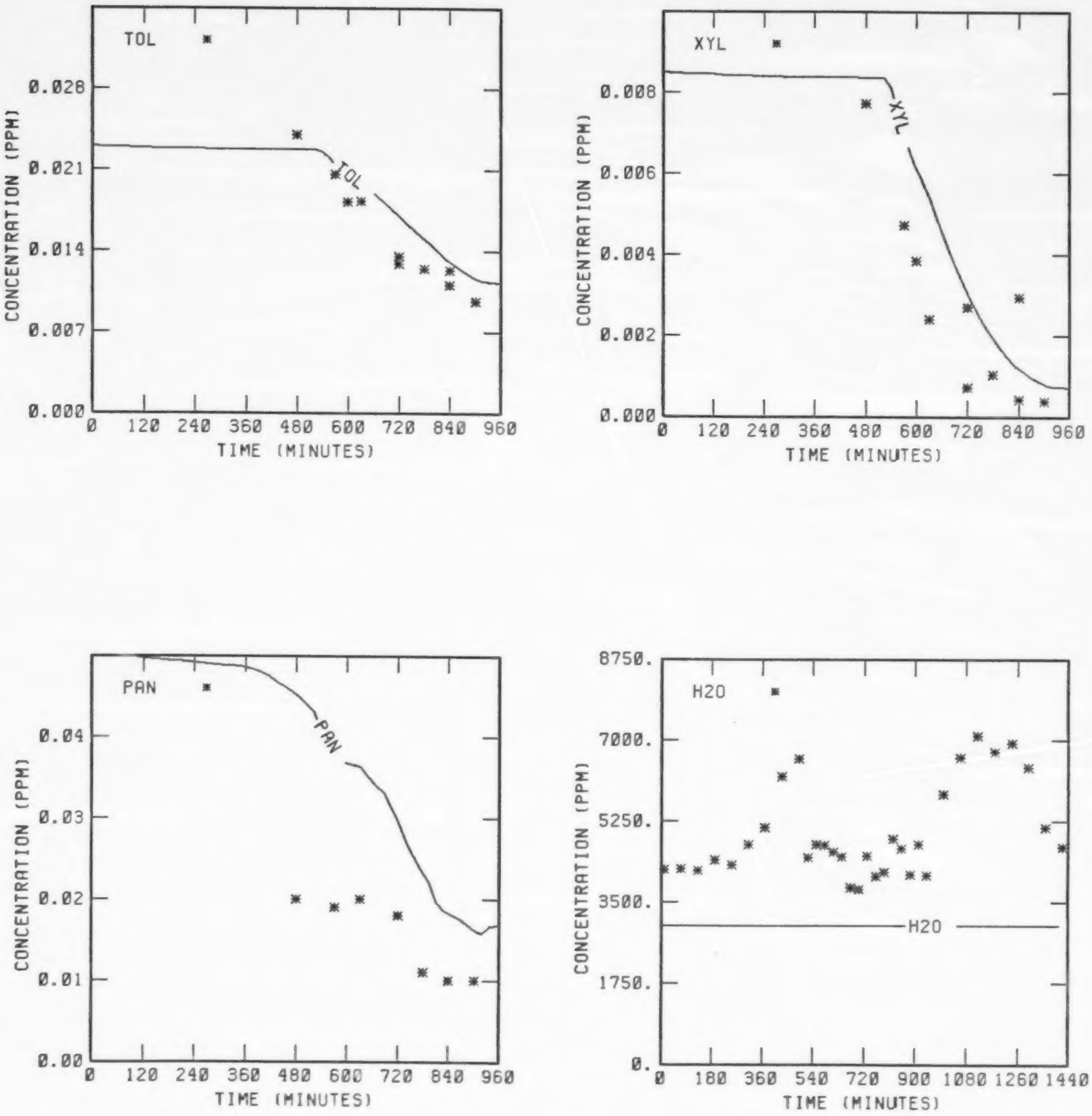


FIGURE **C-15.** SIMULATION RESULTS FOR
OTCR.80383

(continued).

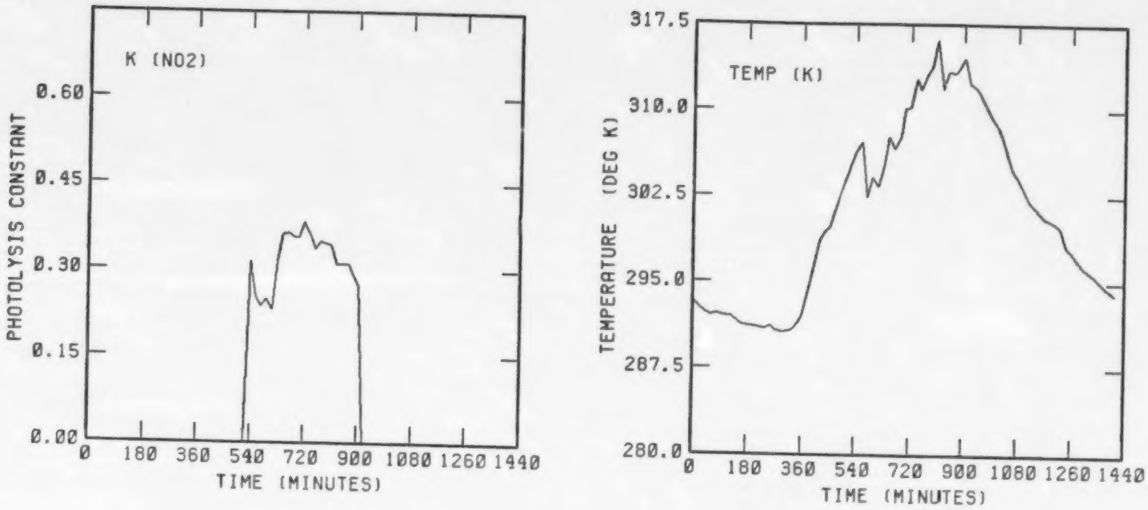


FIGURE **C-15.** SIMULATION RESULTS FOR OTCR.80383 (concluded).

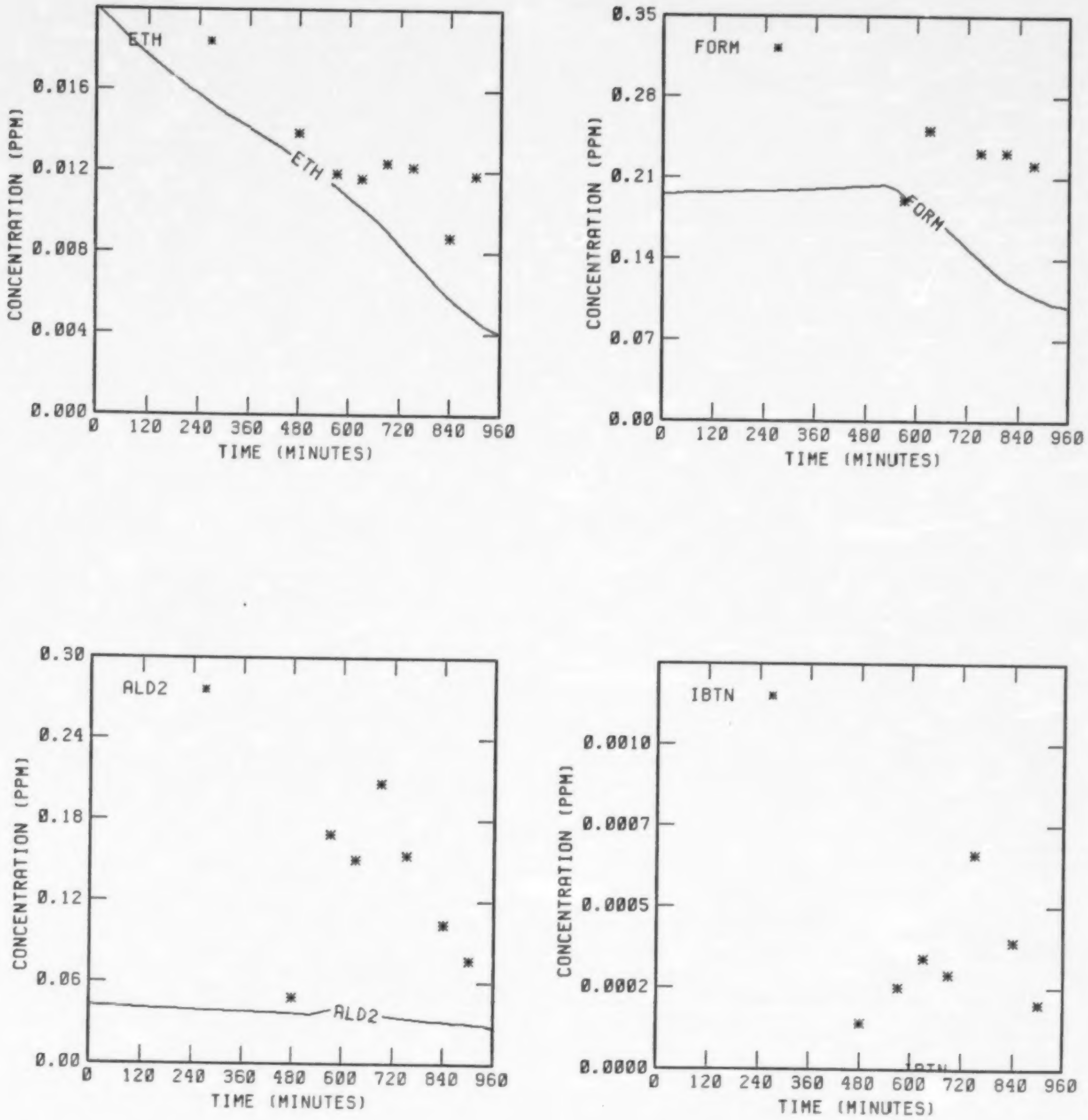


FIGURE **C-16.** SIMULATION RESULTS FOR
OTCR.82583

(continued).

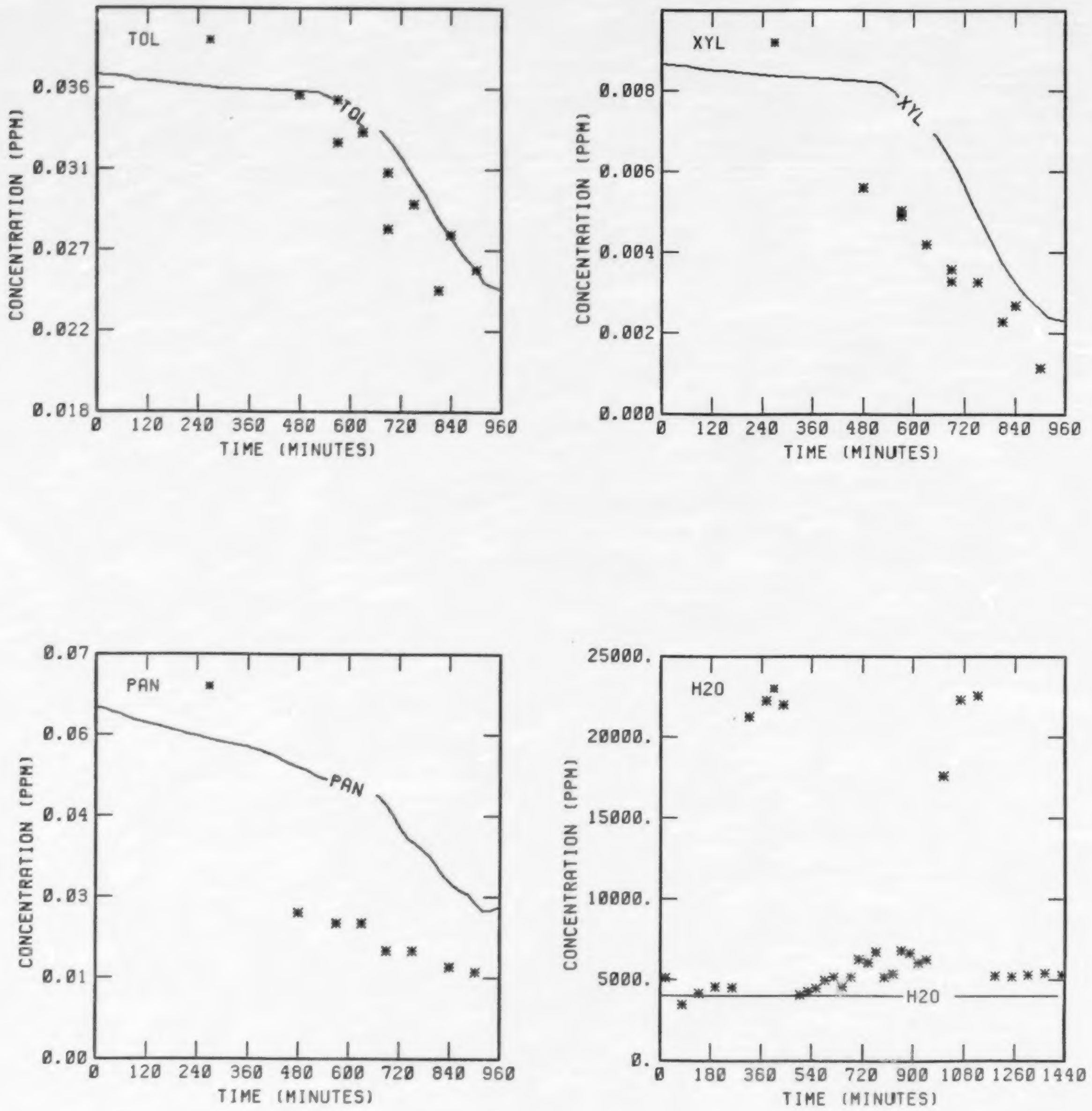


FIGURE C-16. SIMULATION RESULTS FOR
OTCR.82583

(continued).

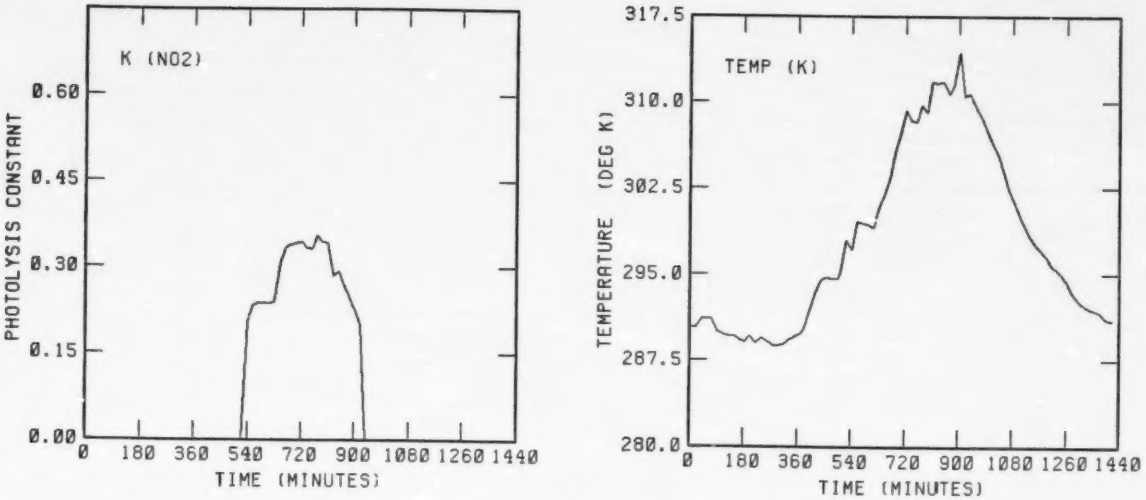


FIGURE C-16. SIMULATION RESULTS FOR
OTCR.82583
(concluded).

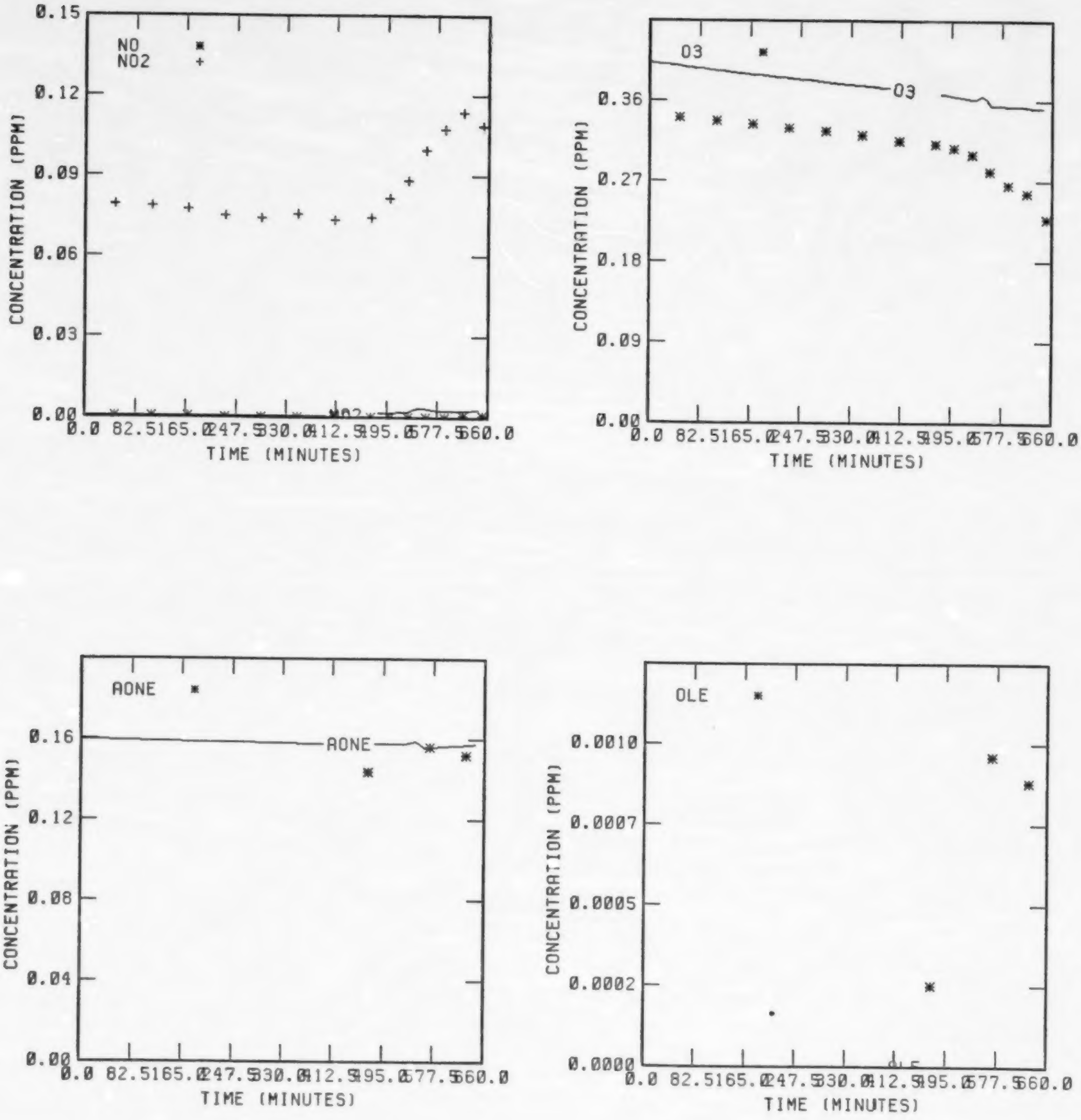


FIGURE C-17. SIMULATION RESULTS FOR
OTCR.82683

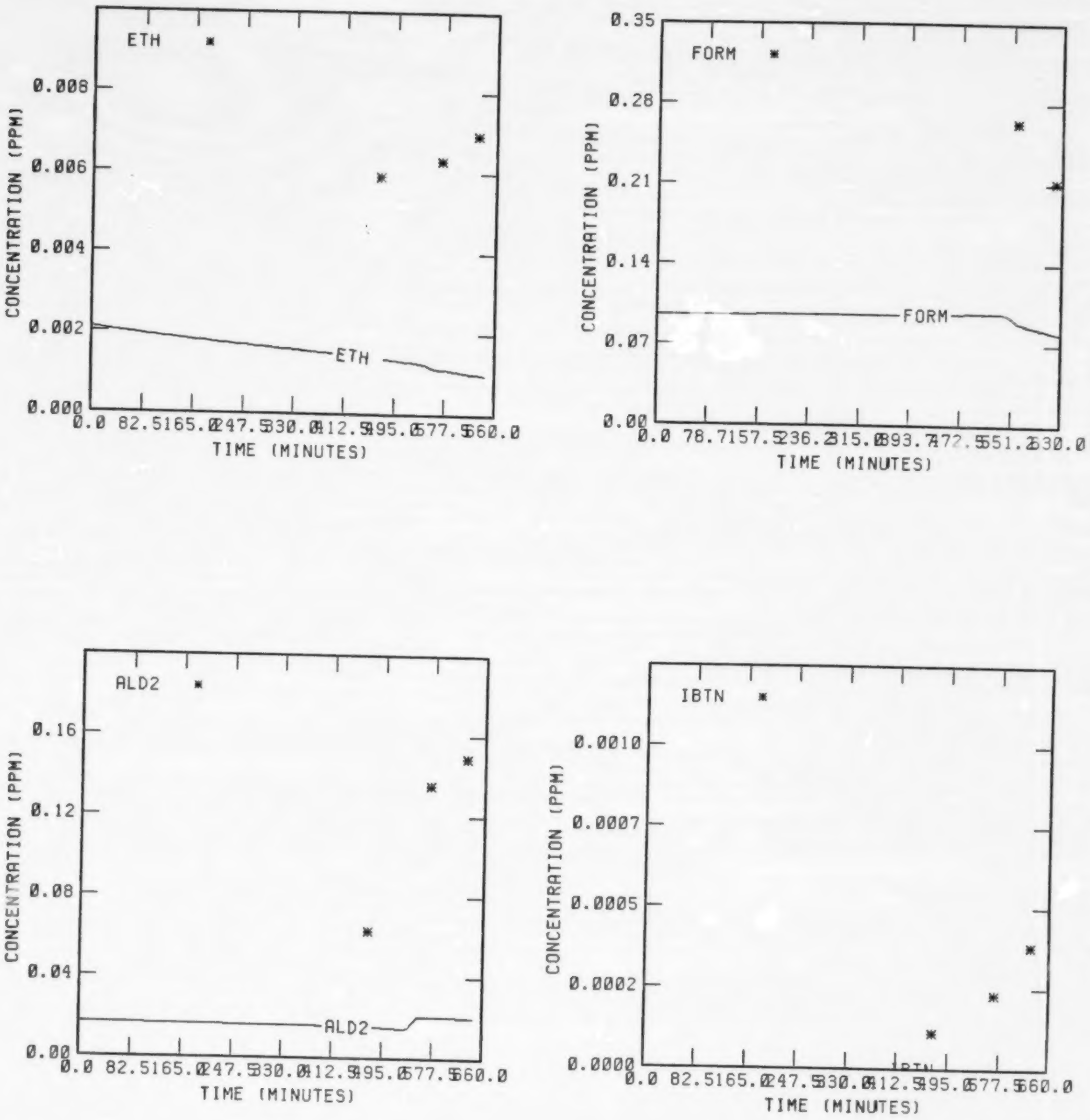


FIGURE C-17. SIMULATION RESULTS FOR
OTCR.82683
(continued).

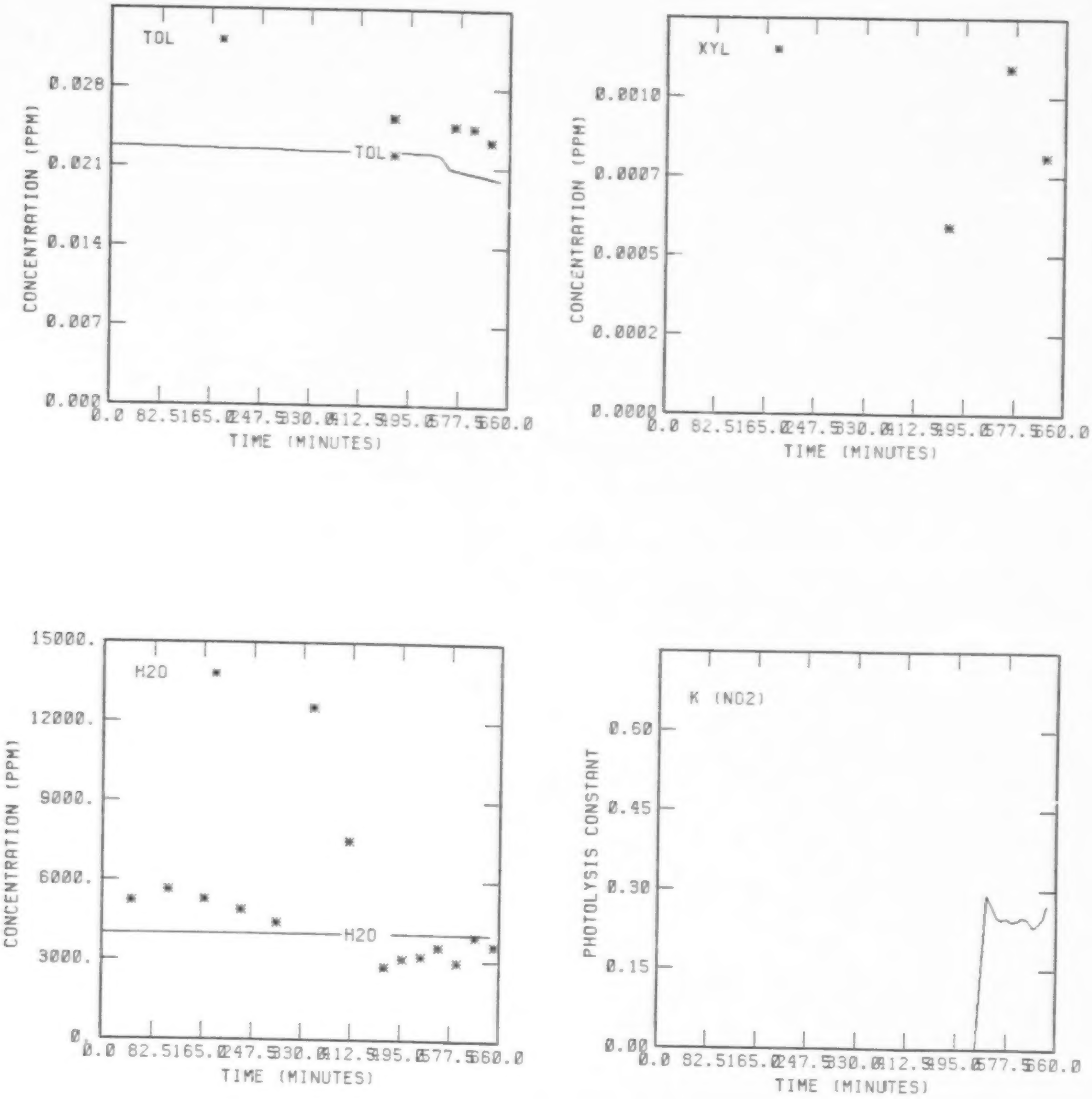


FIGURE C-17. SIMULATION RESULTS FOR
OTCR.82683
(continued).

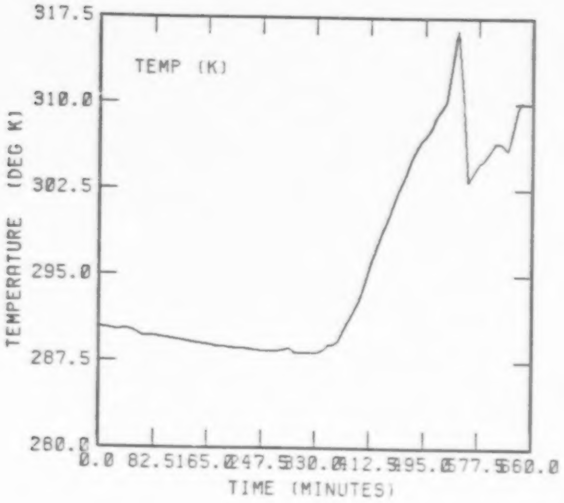


FIGURE **C-17.** SIMULATION RESULTS FOR OTCR.82683 (concluded).

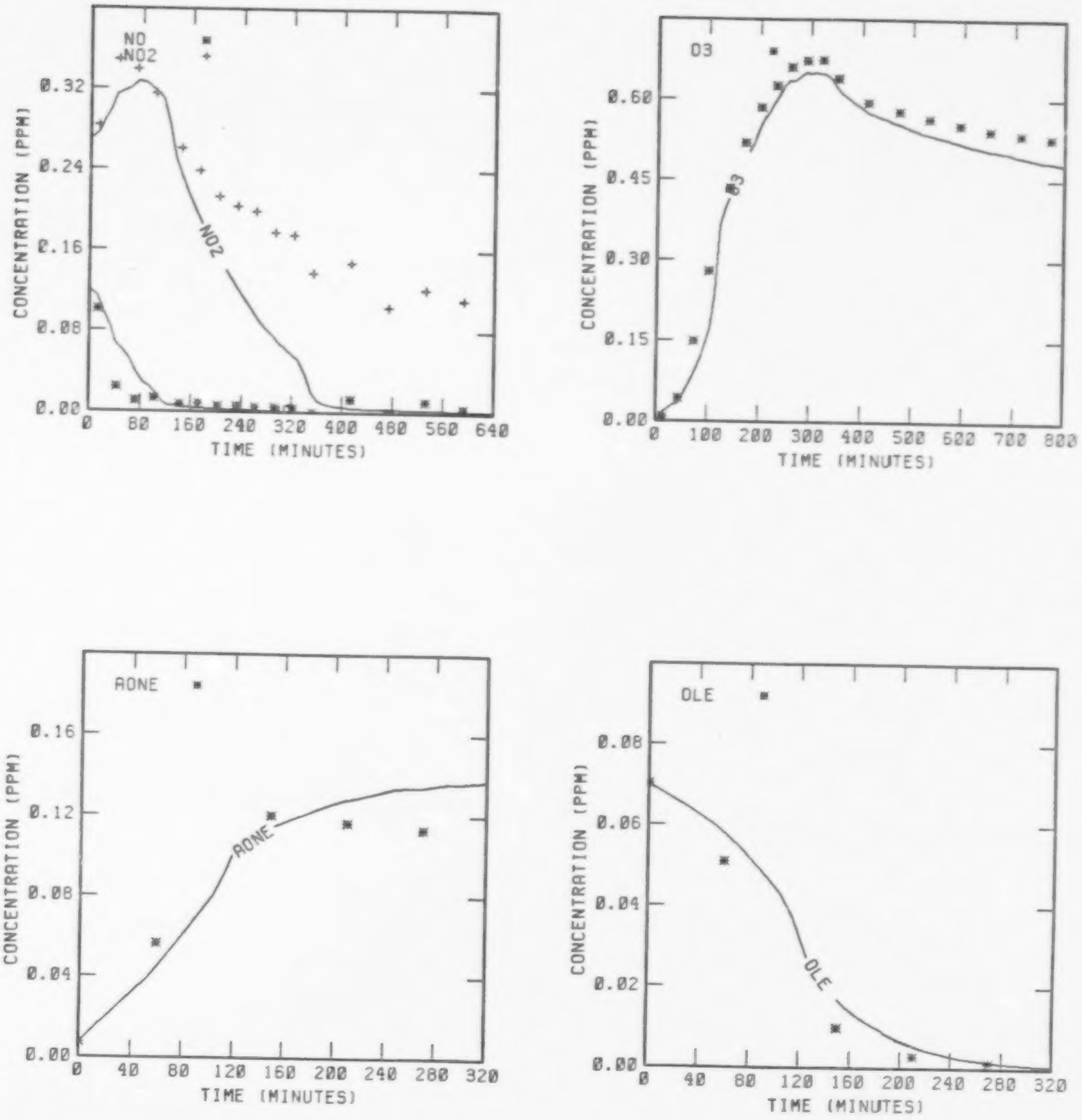


FIGURE C-18. SIMULATION RESULTS FOR OTCB.83083

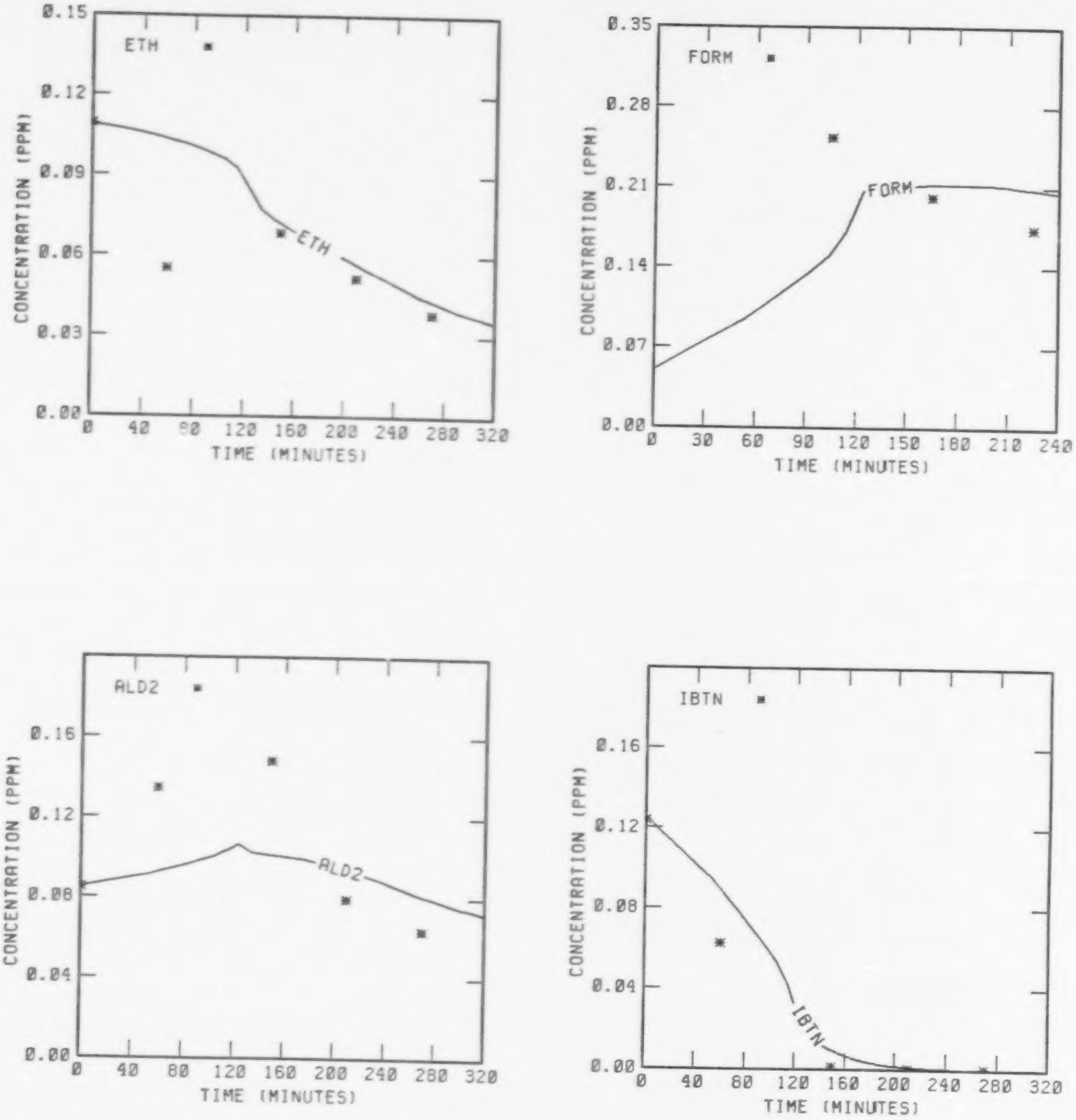


FIGURE C-18. SIMULATION RESULTS FOR OTCB.83083 (continued).

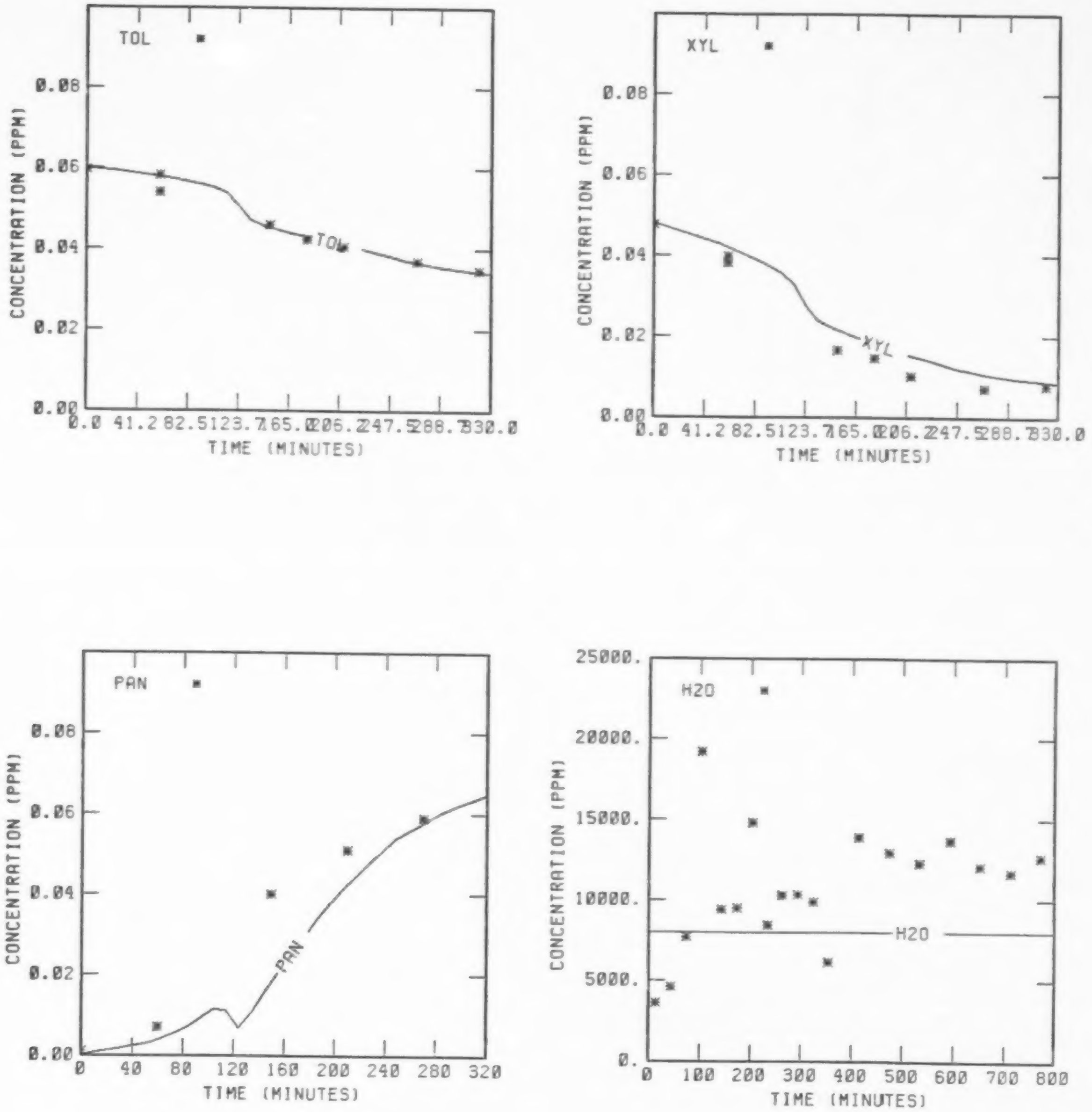


FIGURE C-18. SIMULATION RESULTS FOR
OTCB.83083
(continued).

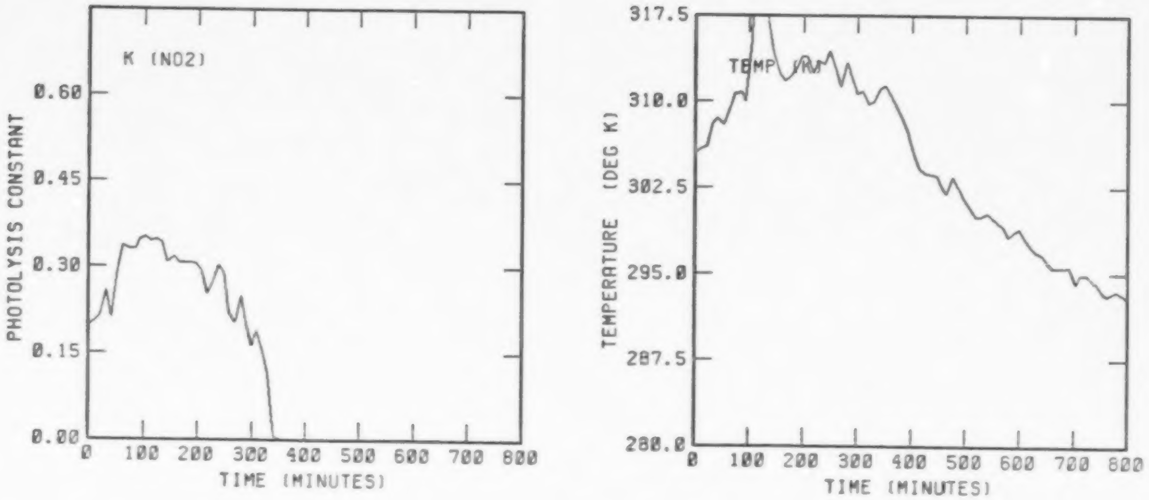


FIGURE C-18. SIMULATION RESULTS FOR OTCB.83083 (concluded).

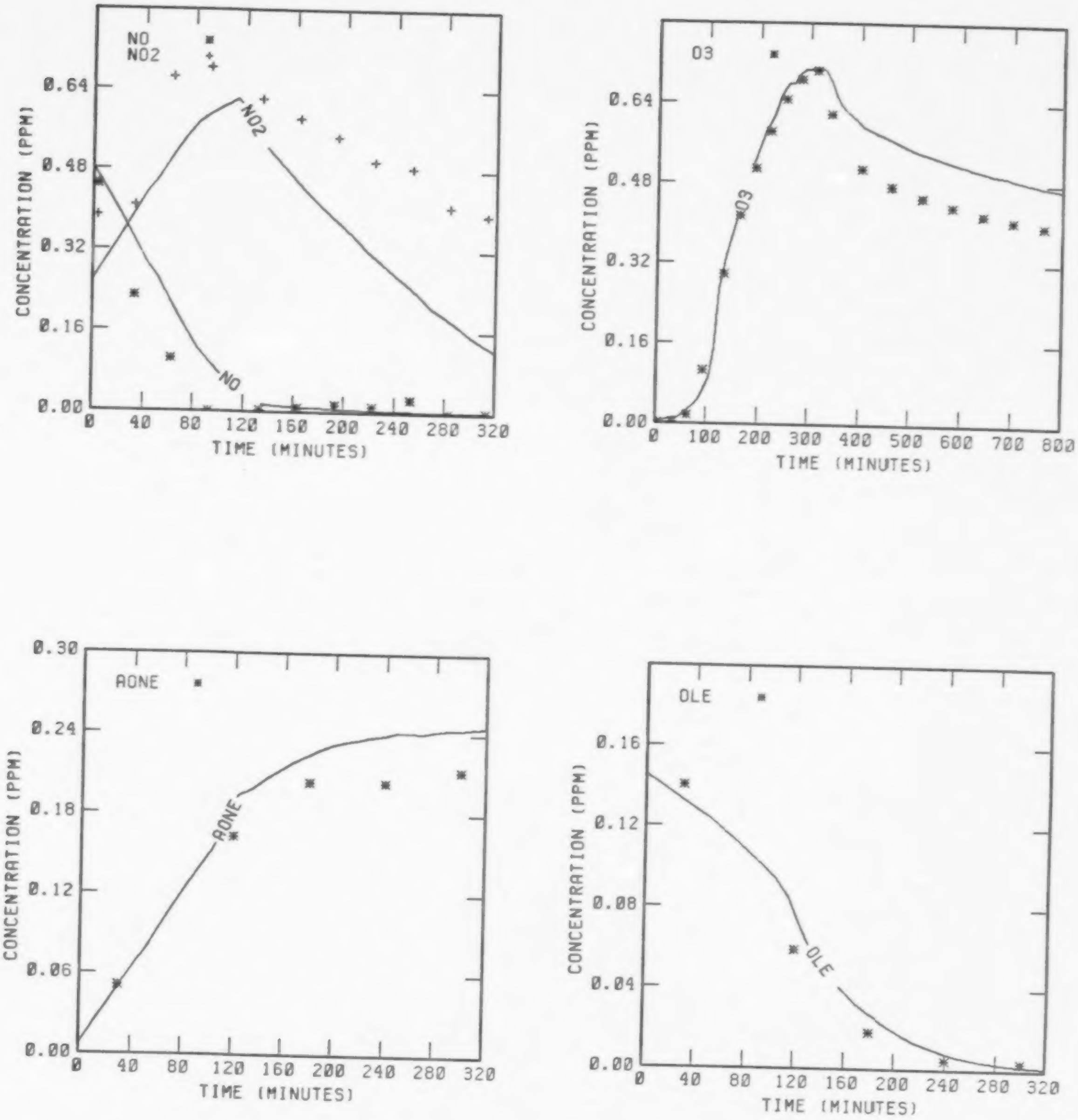


FIGURE C-19. SIMULATION RESULTS FOR OTCR.83083

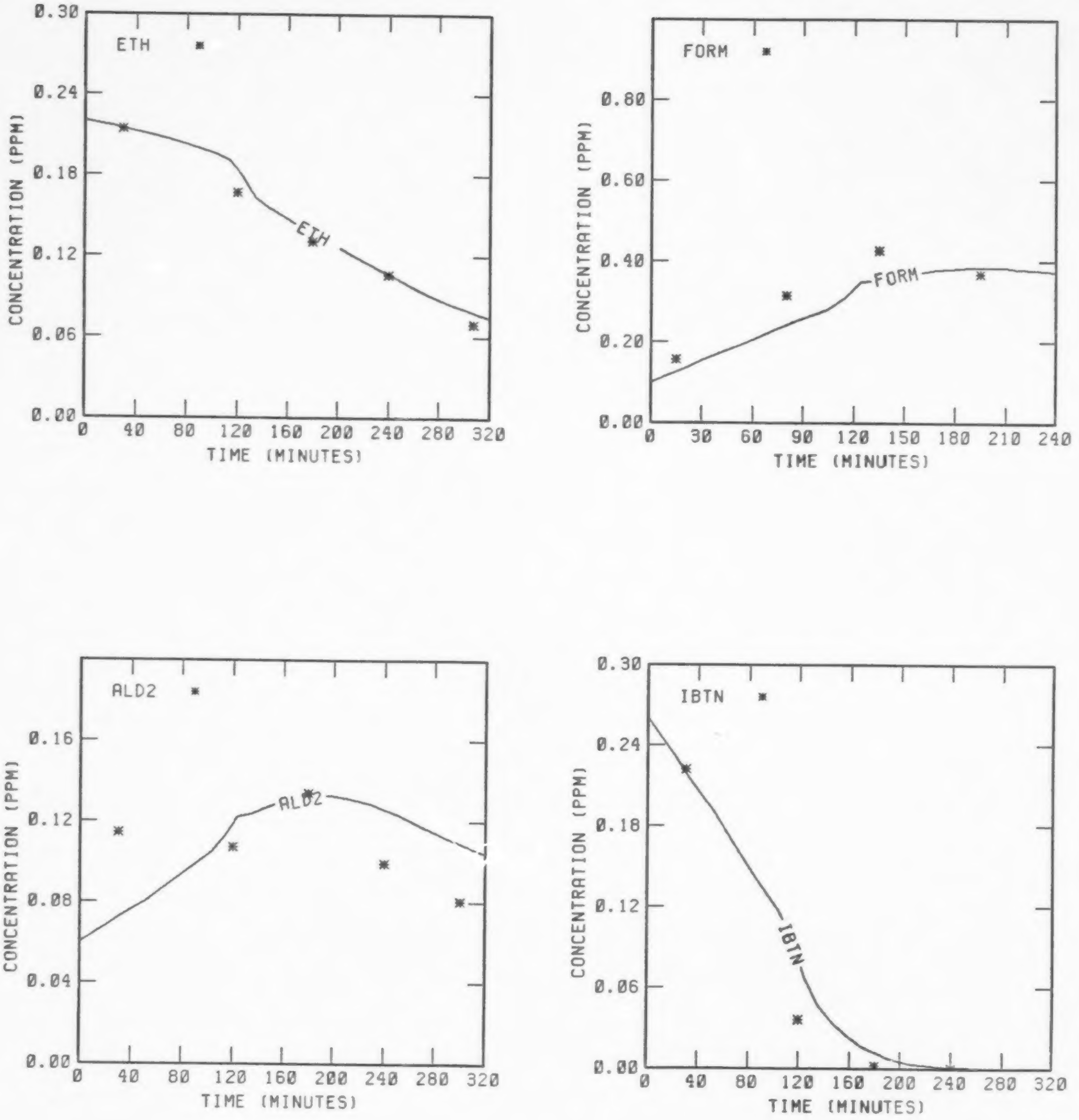


FIGURE C-19. SIMULATION RESULTS FOR OTCR.83083 (continued).

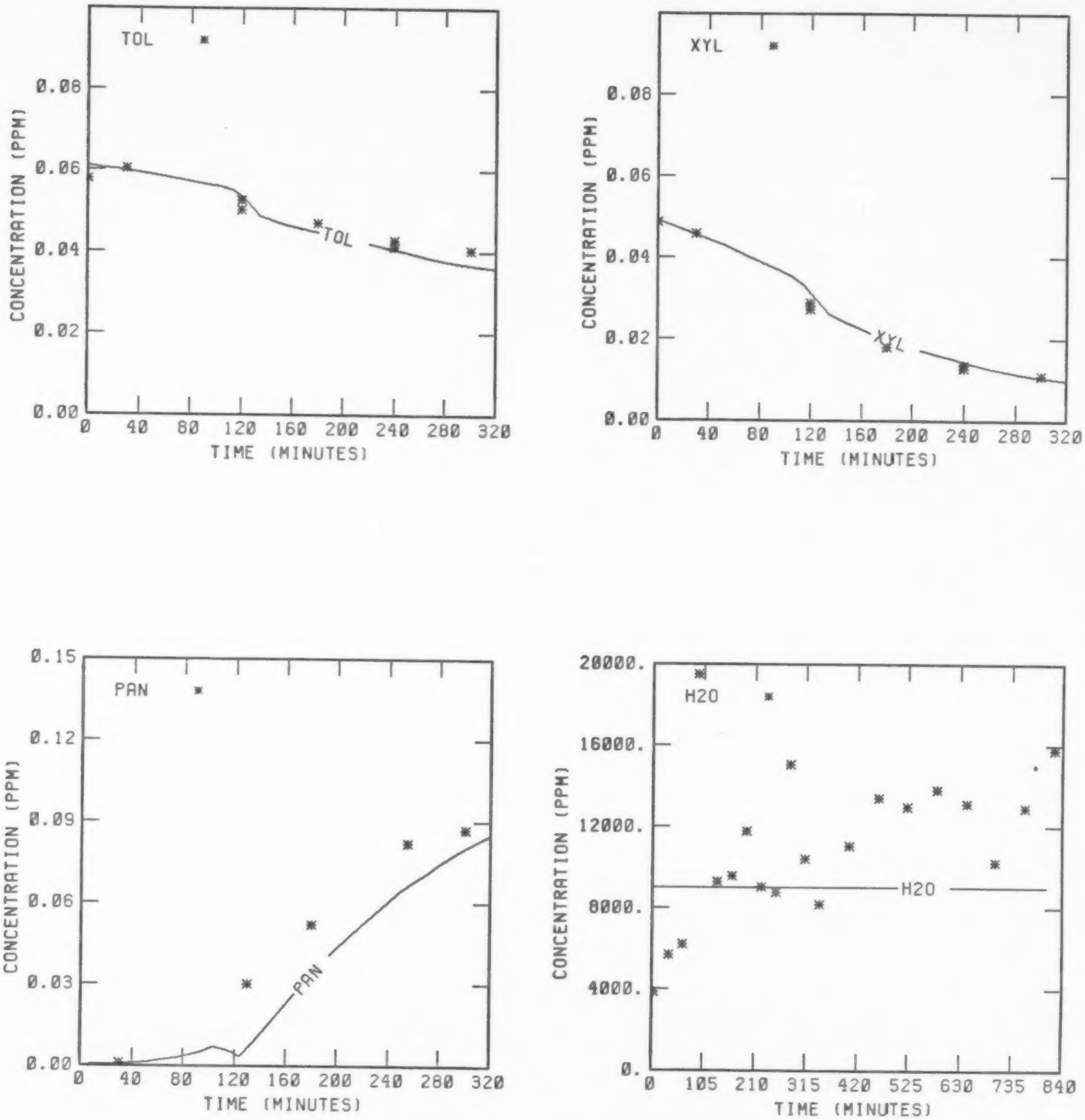


FIGURE C-19. SIMULATION RESULTS FOR
OTCR.83083
(continued).

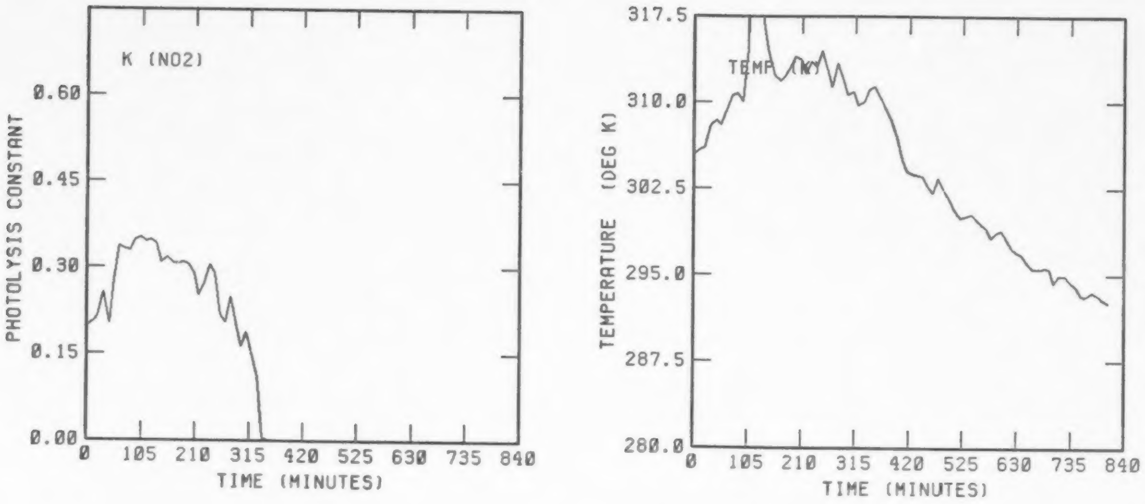


FIGURE C-19. SIMULATION RESULTS FOR
OTCR.83083

(concluded).

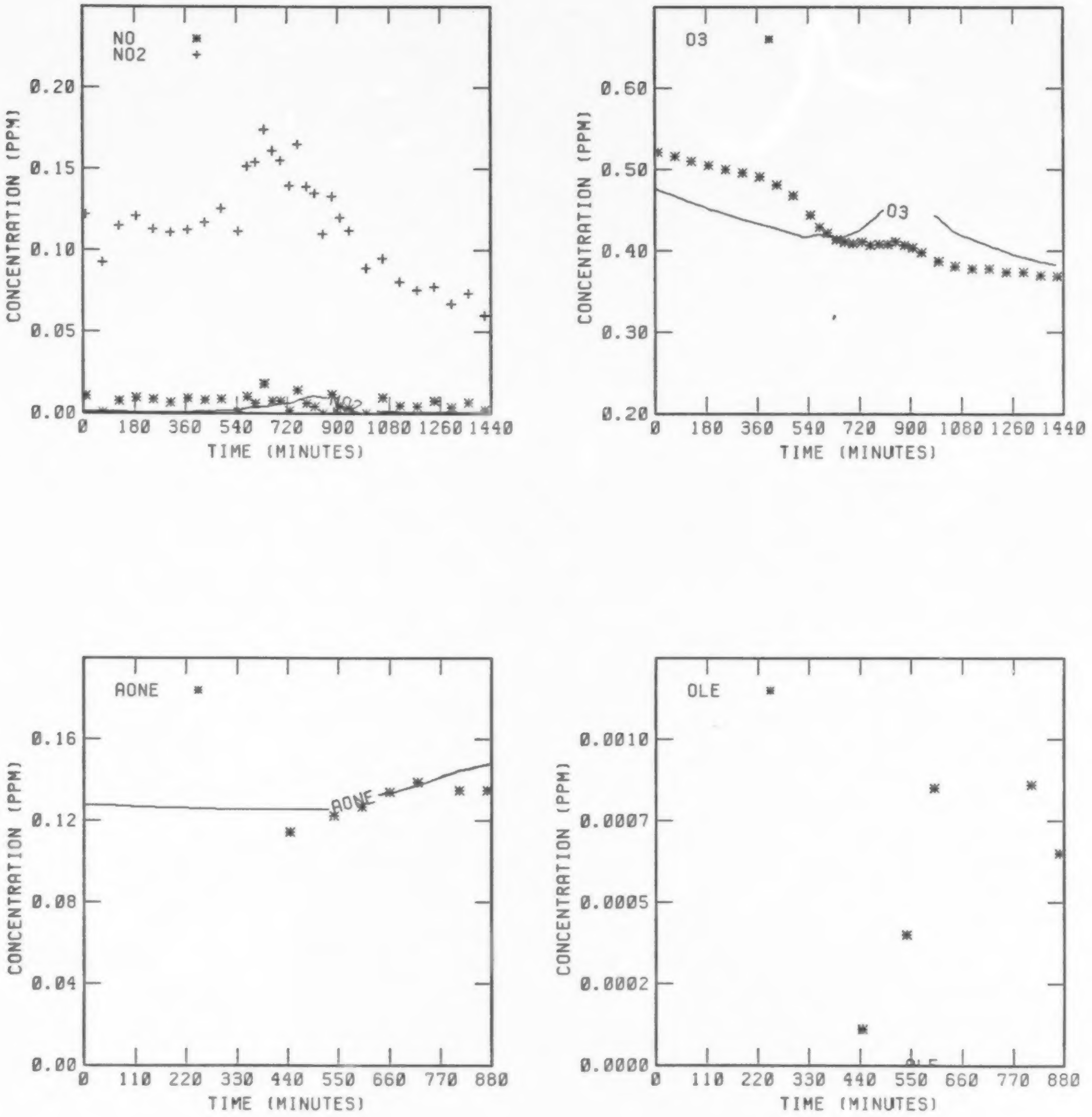


FIGURE C-20. SIMULATION RESULTS FOR OTCB.83183

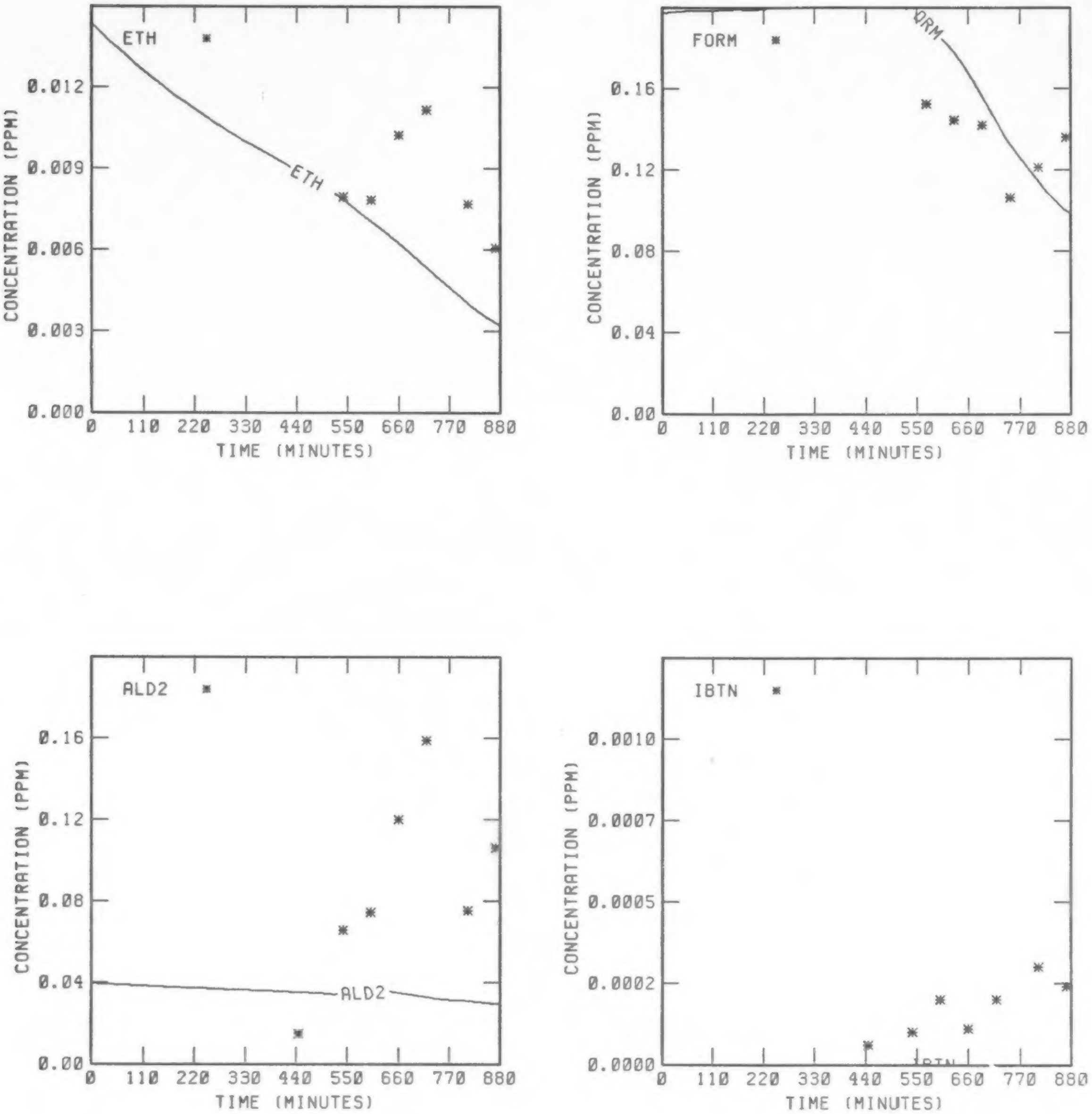


FIGURE C-20. SIMULATION RESULTS FOR
OTCB.83183
(continued).

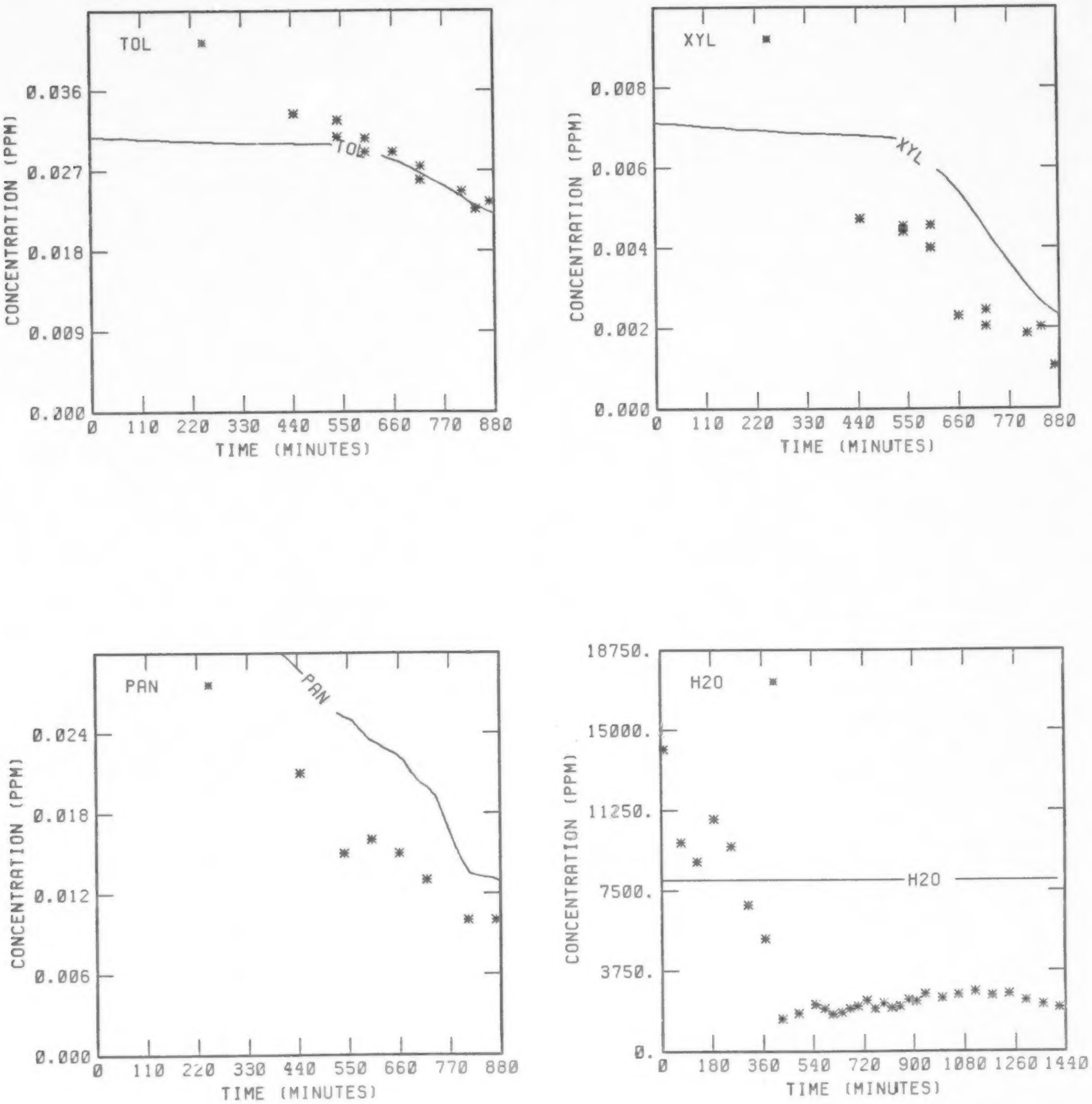


FIGURE C-20. SIMULATION RESULTS FOR
OTCB.83183
(continued).

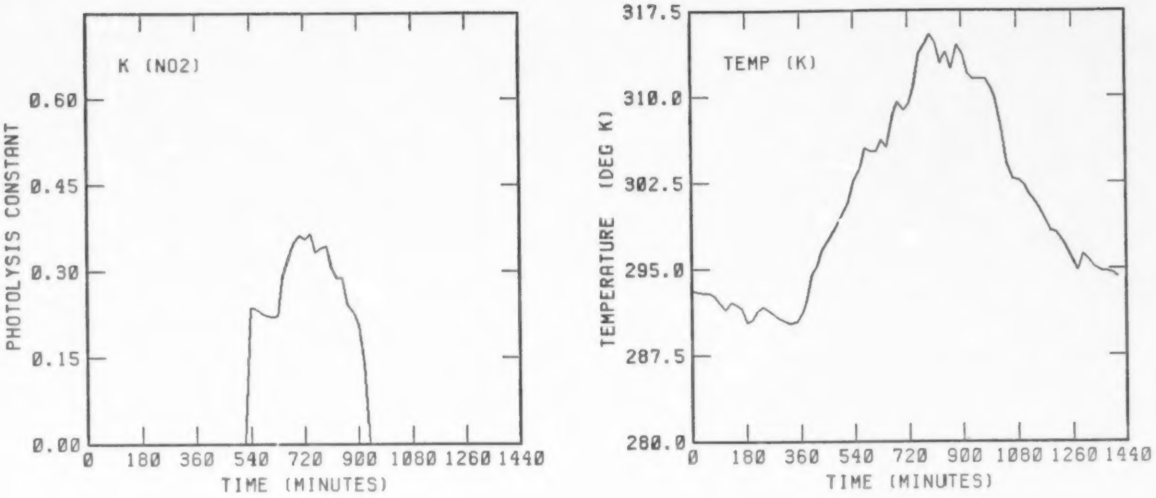


FIGURE C-20. SIMULATION RESULTS FOR
OTCB.83183

(concluded).

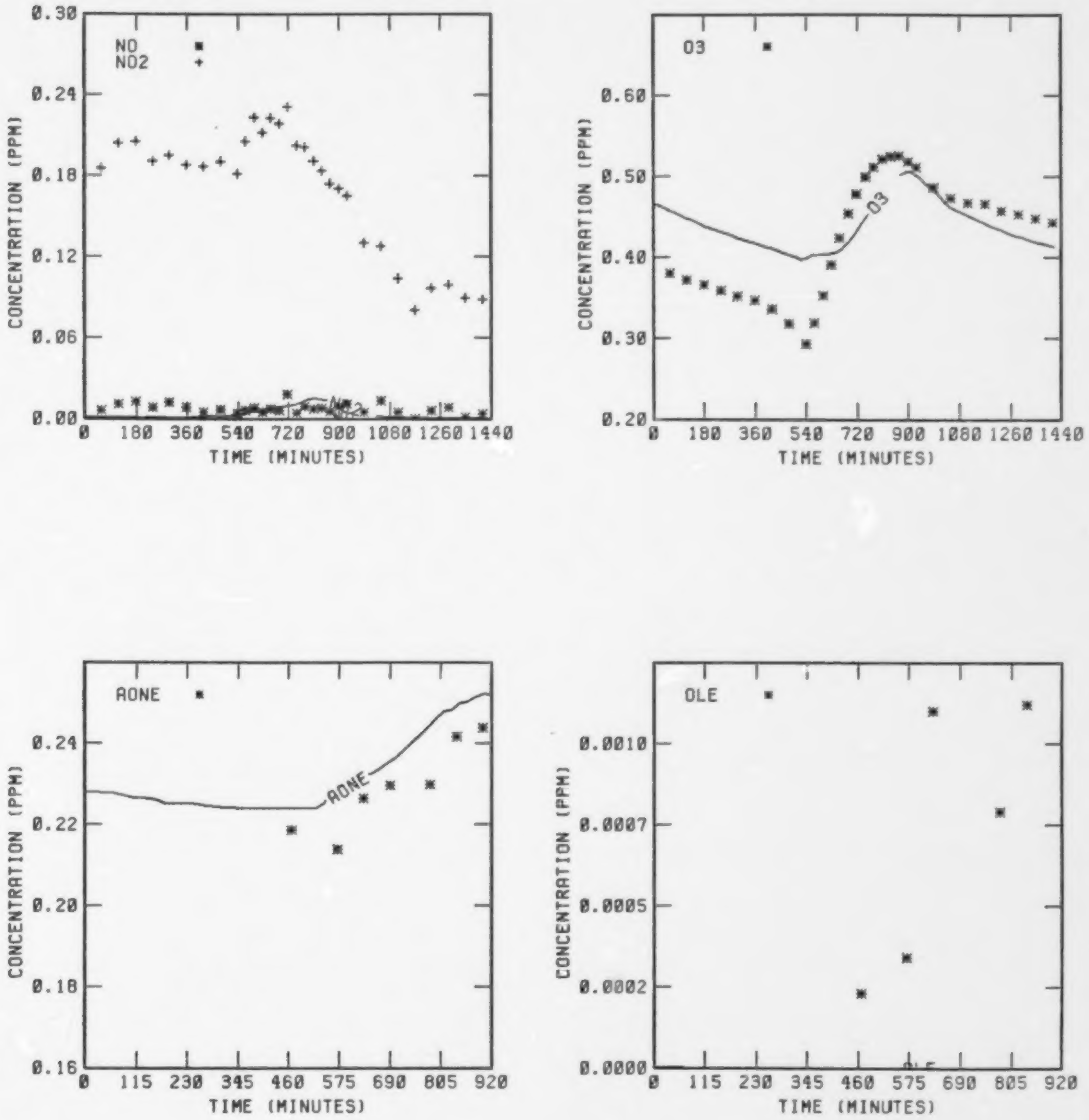


FIGURE C-21. SIMULATION RESULTS FOR
OTCR.83183

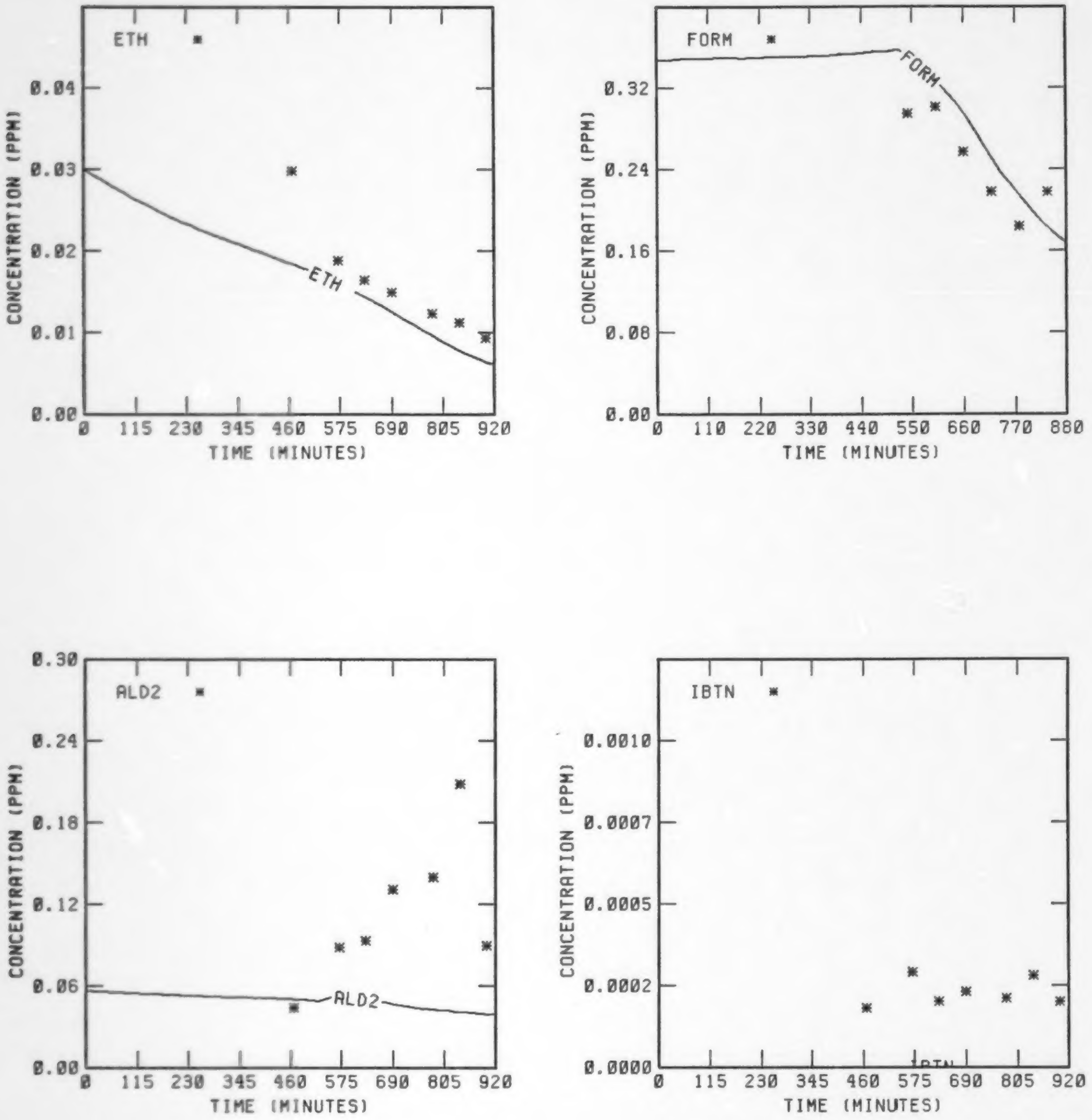


FIGURE C-21. SIMULATION RESULTS FOR
OTCR.83183
(continued).

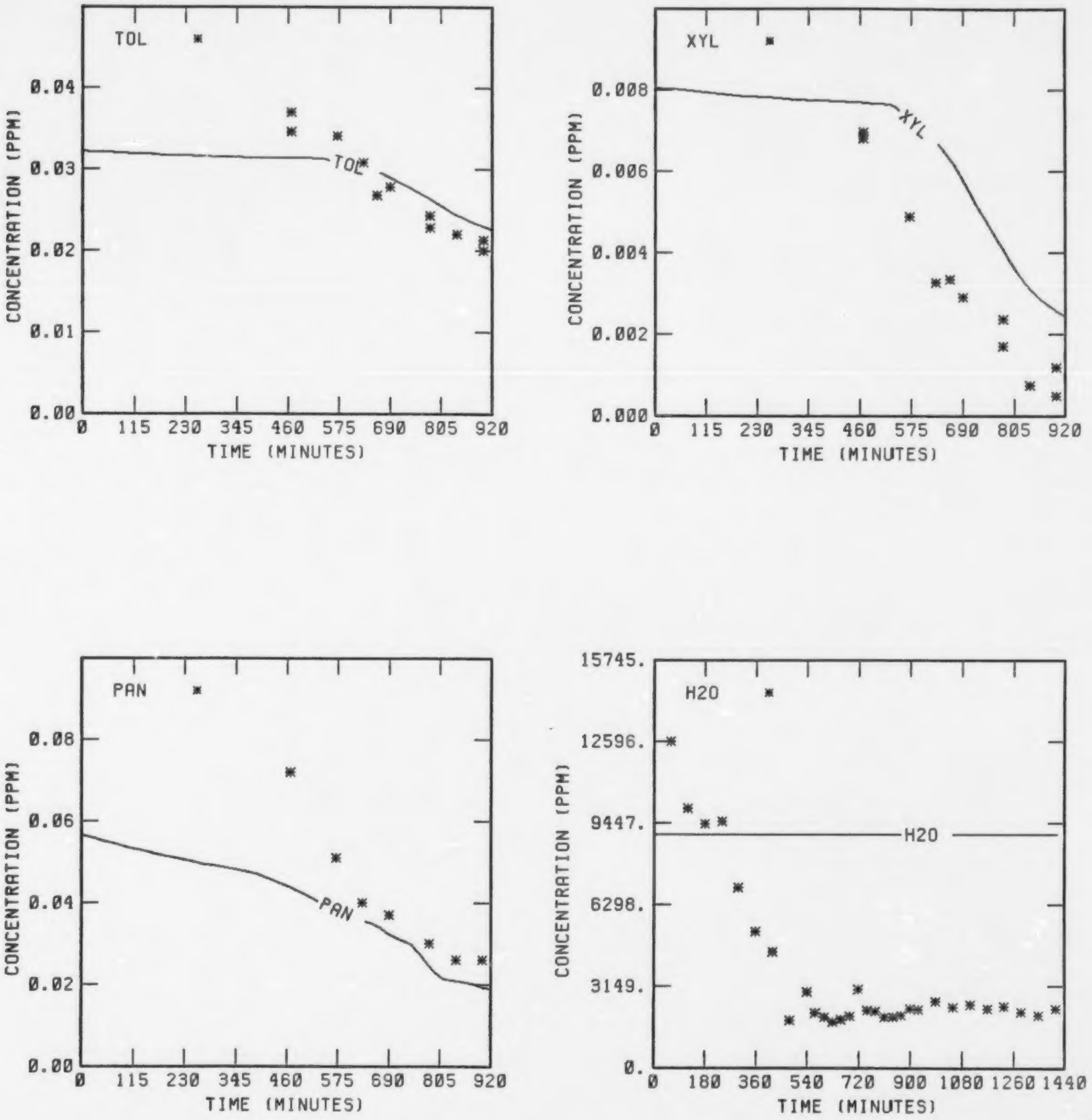


FIGURE C-21. SIMULATION RESULTS FOR OTCR.83183

(continued).

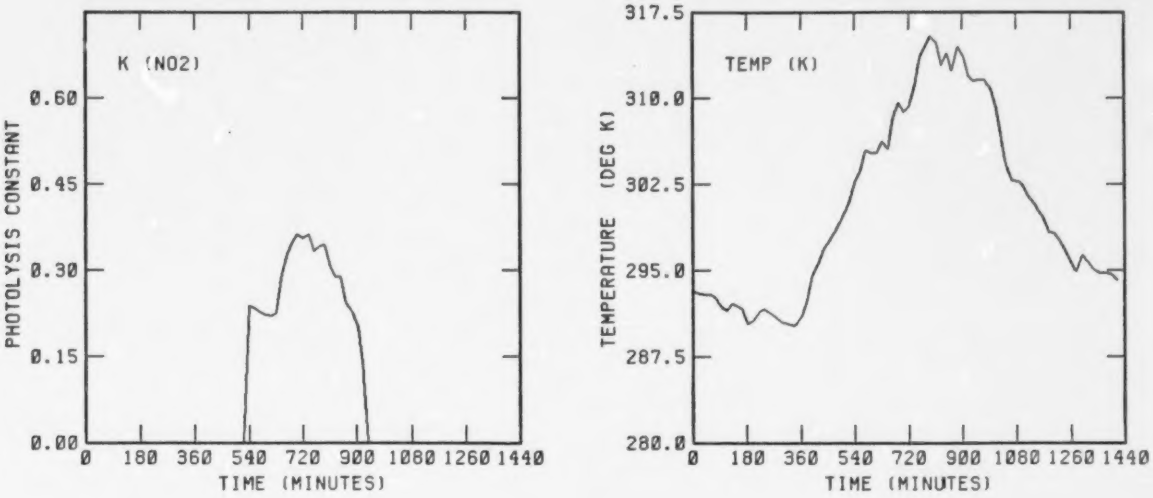


FIGURE C-21. SIMULATION RESULTS FOR OTCR.83183 (concluded).

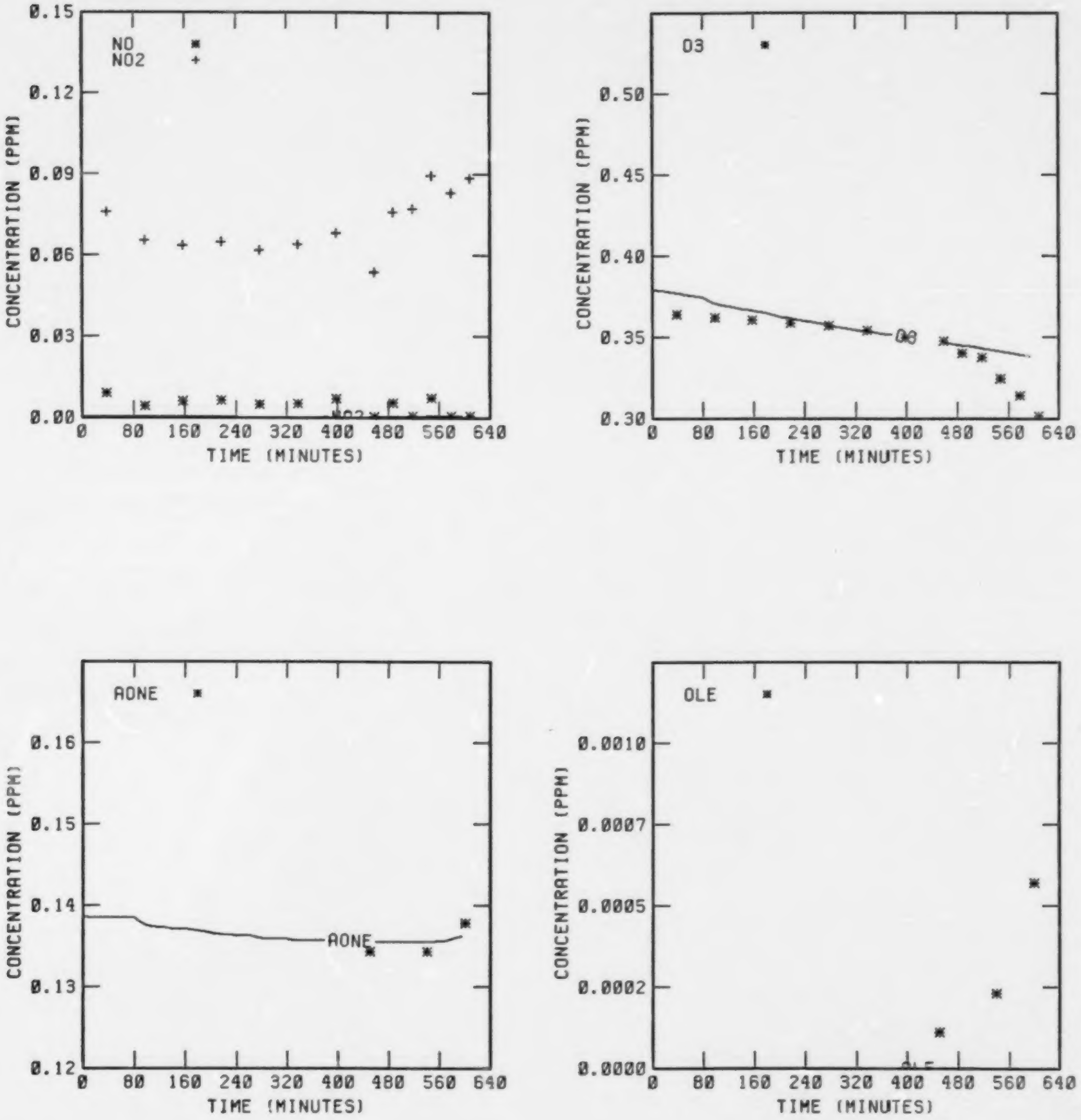


FIGURE C-22. SIMULATION RESULTS FOR
OTCB.90183

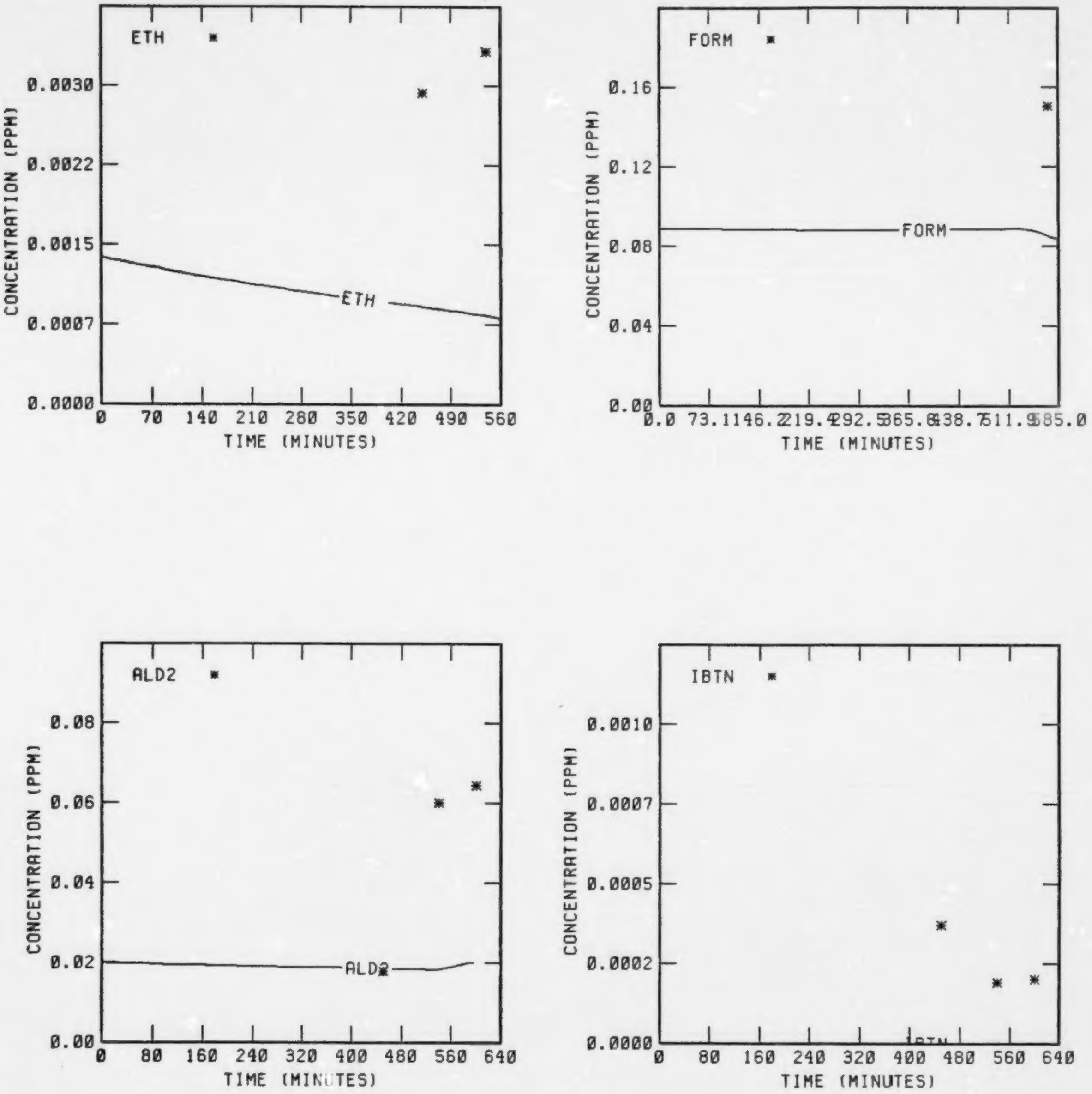


FIGURE C-22. SIMULATION RESULTS FOR OTCB.90183 (continued).

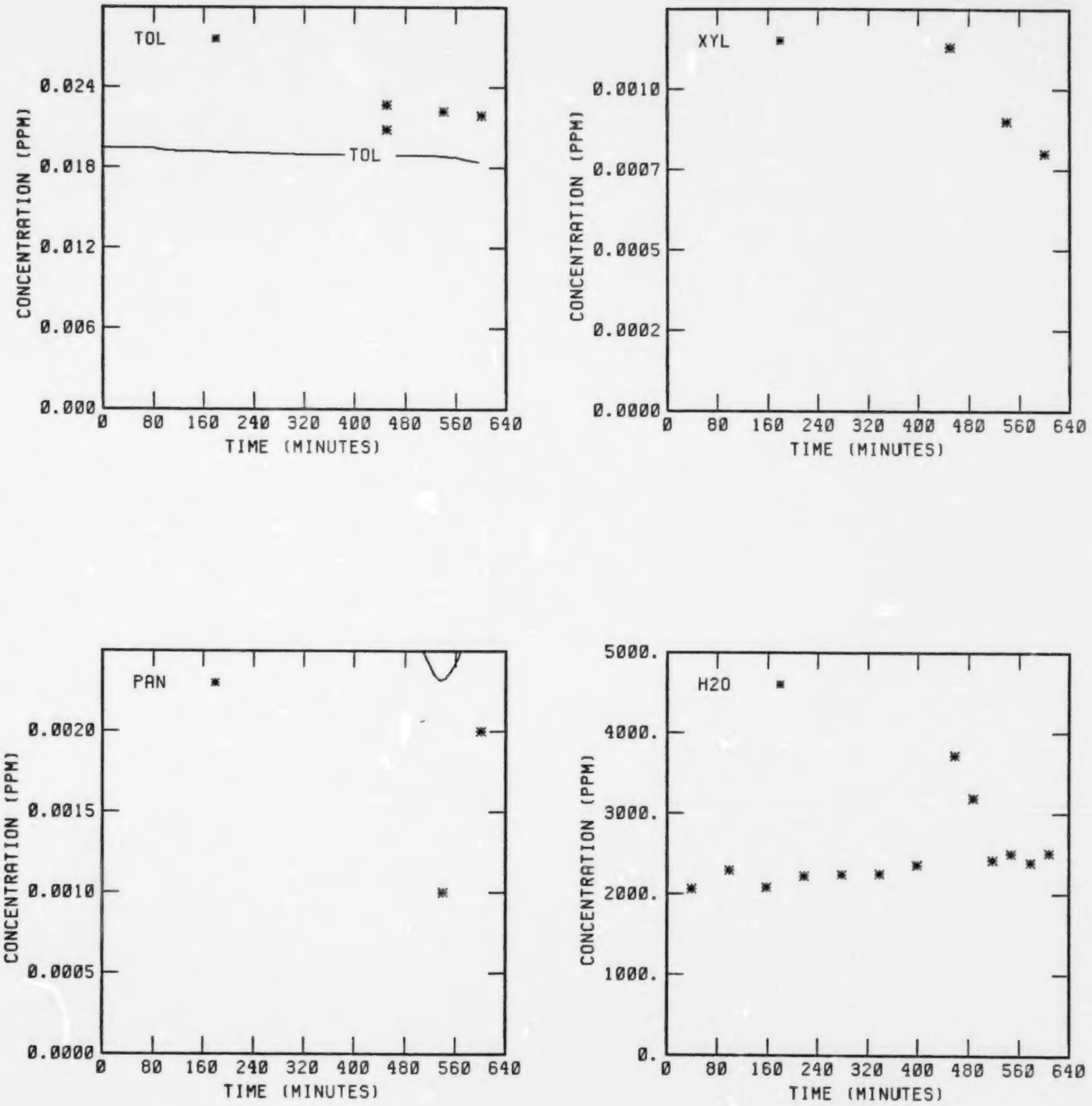


FIGURE C-22. SIMULATION RESULTS FOR
OTCB.90183
(continued).

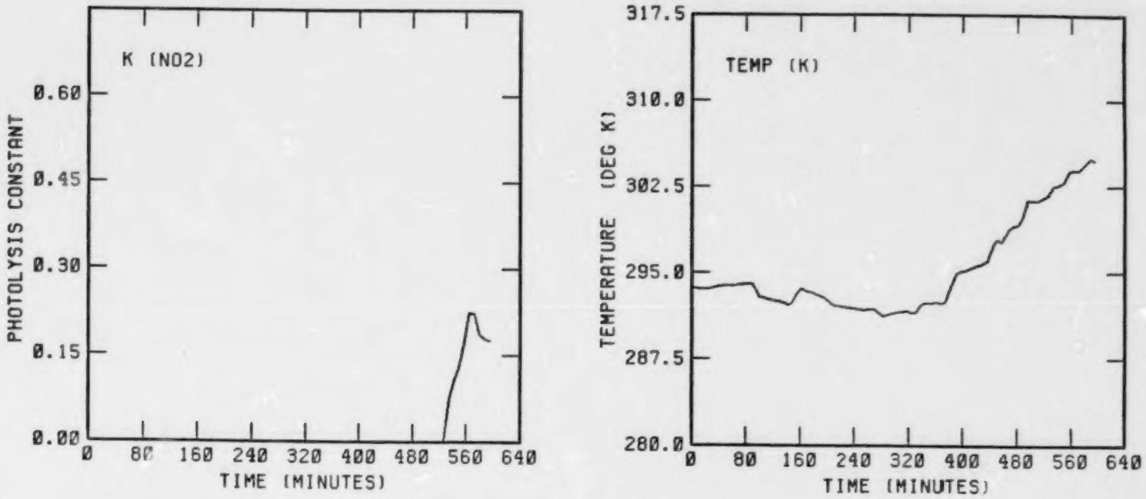


FIGURE C-22. SIMULATION RESULTS FOR OTCB.90183

(concluded).

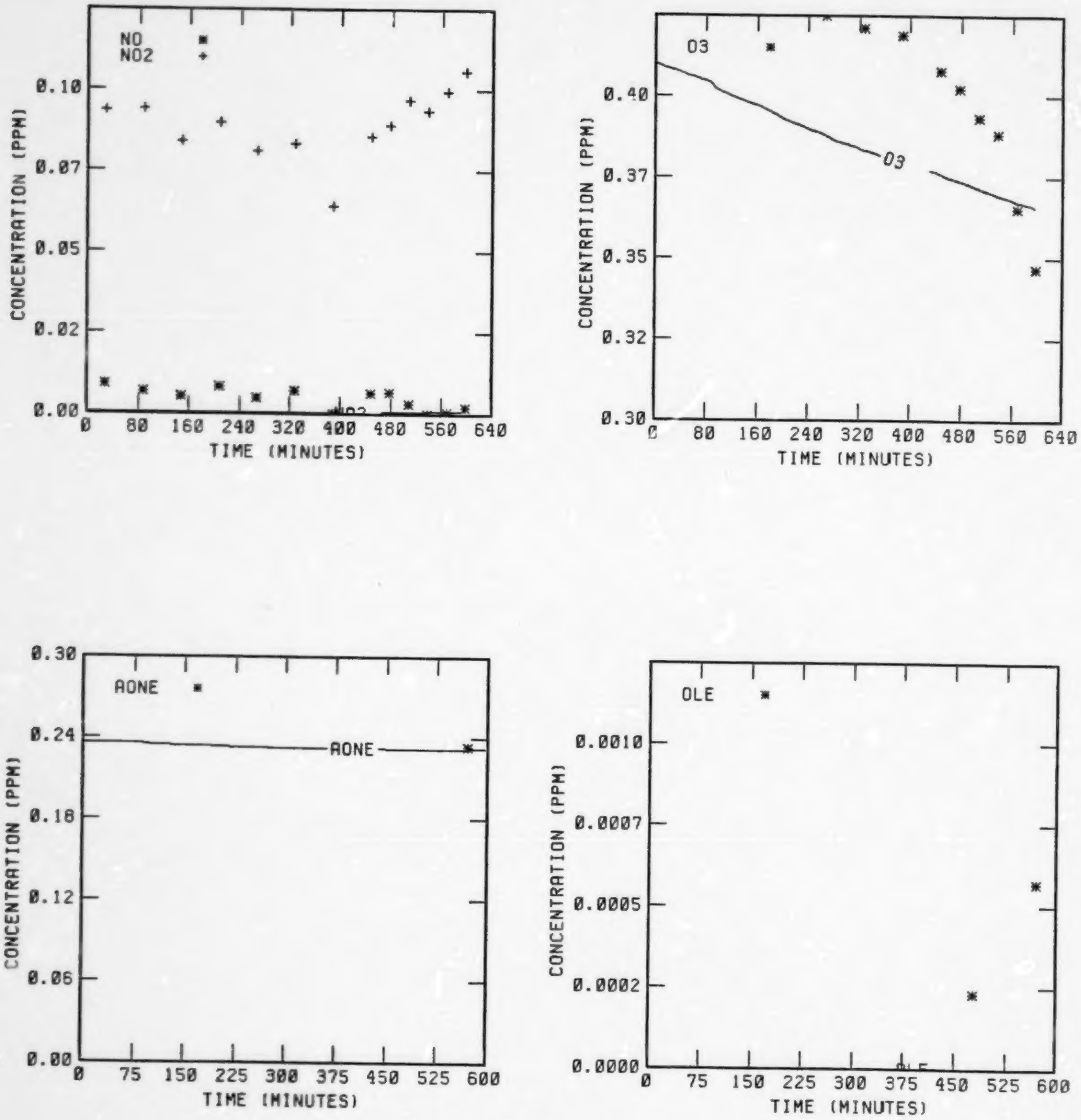


FIGURE C-23. SIMULATION RESULTS FOR OTCR.90183

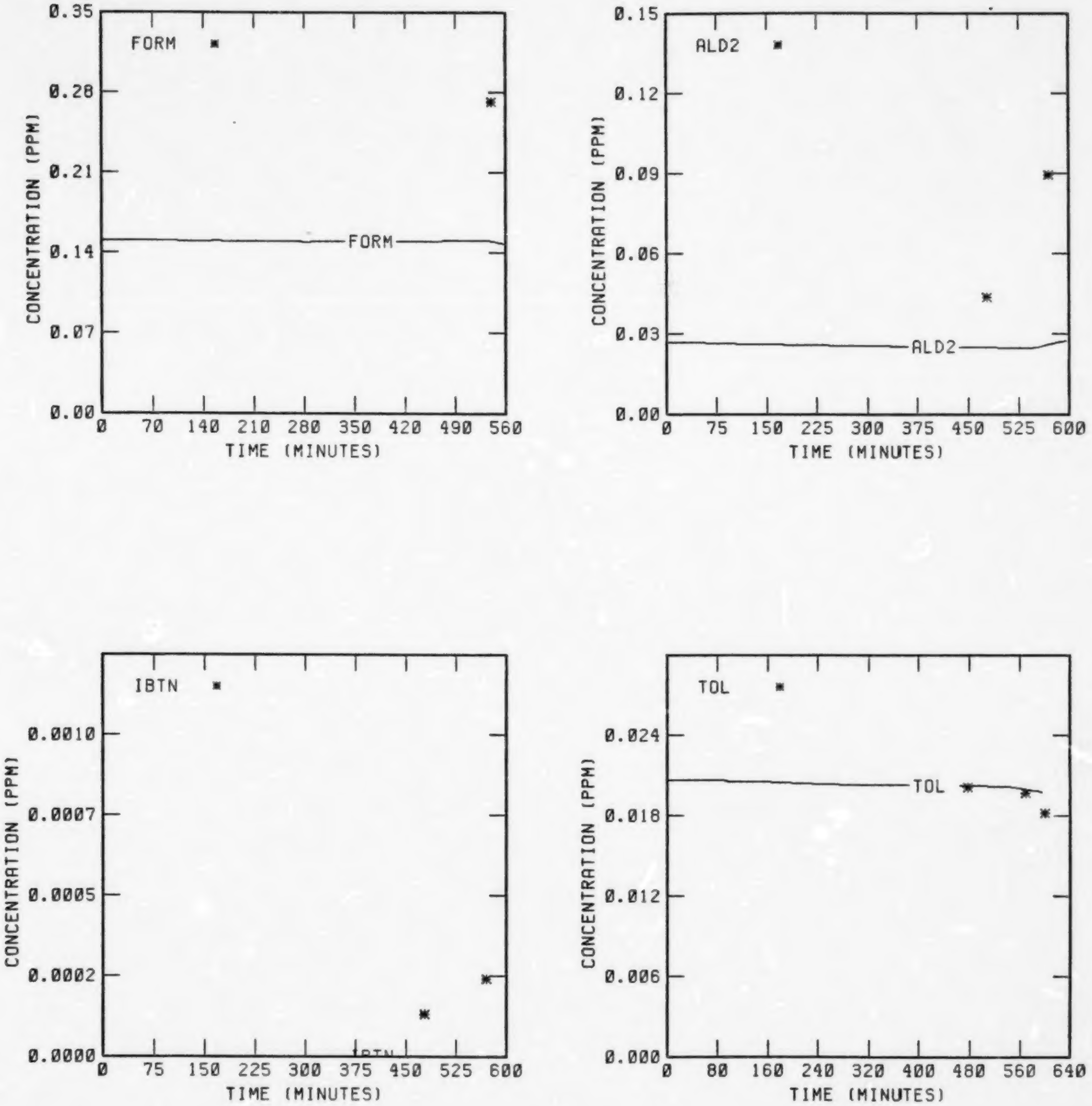


FIGURE C-23. SIMULATION RESULTS FOR
OTCR.90183
(continued).

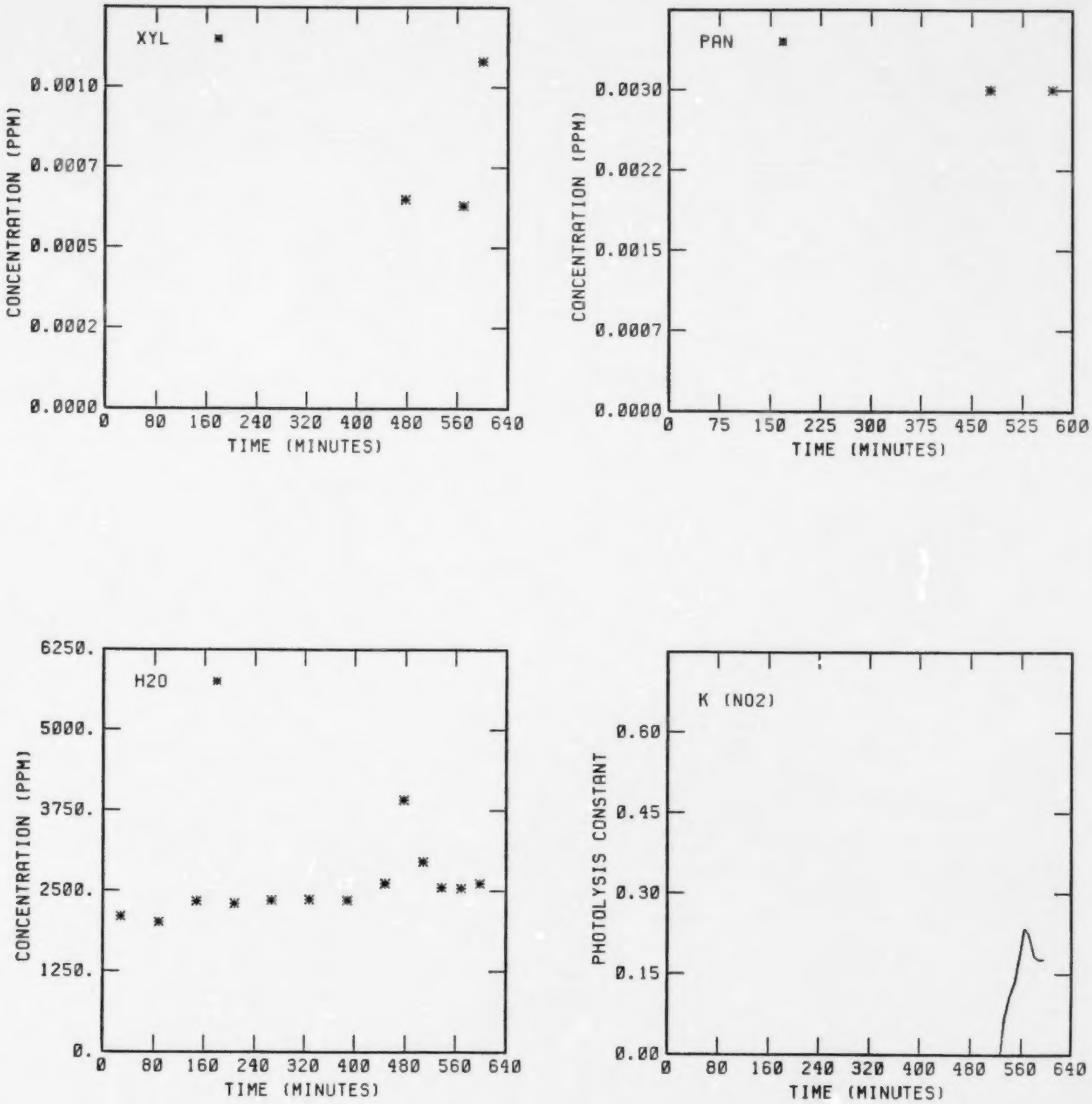


FIGURE C-23. SIMULATION RESULTS FOR OTCR.90183 (continued).

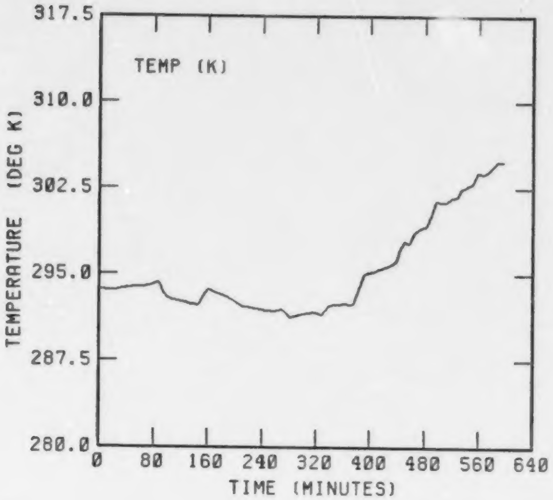


FIGURE C-23. SIMULATION RESULTS FOR
OTCR.90183
(concluded).

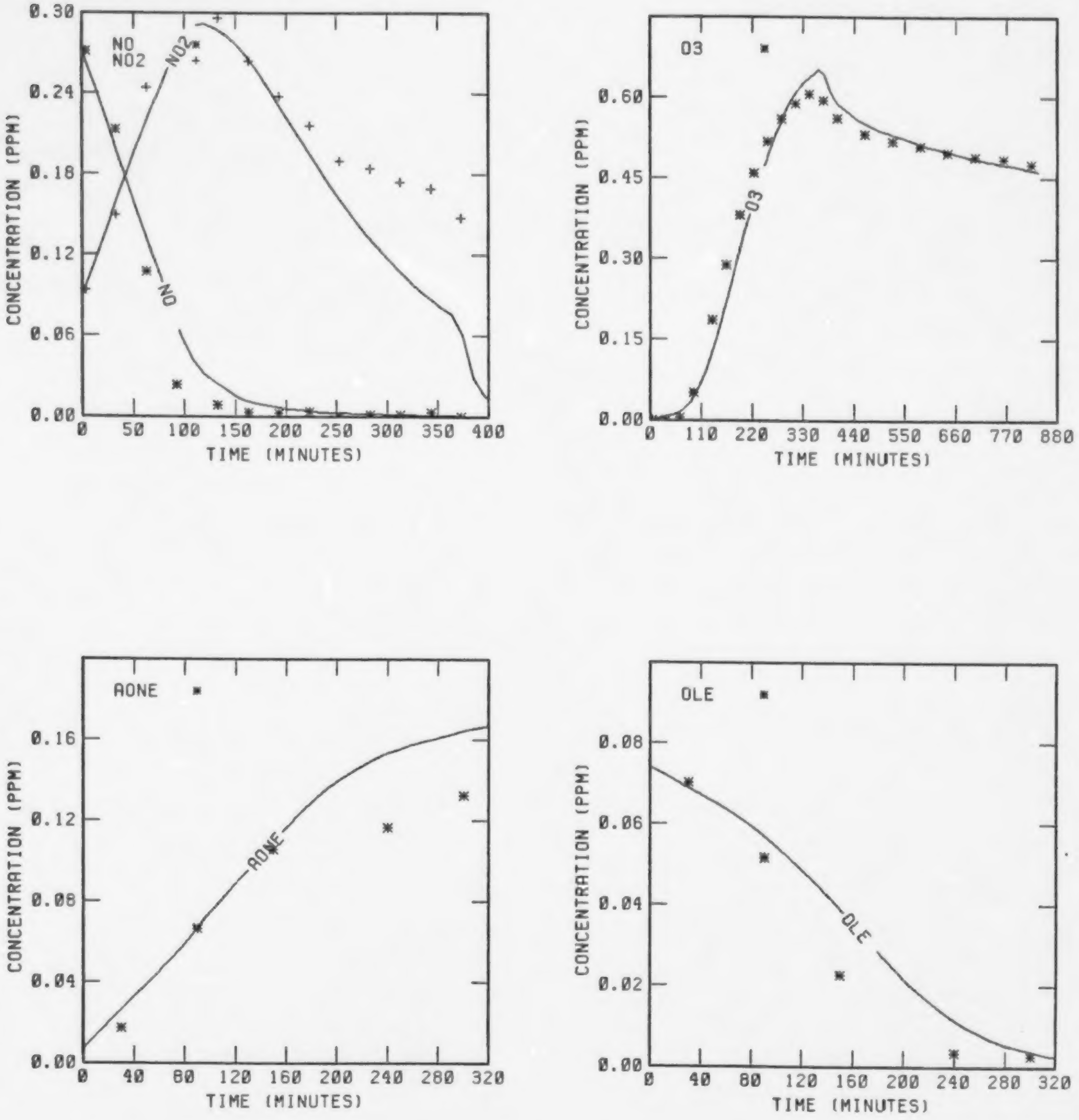


FIGURE C-24. SIMULATION RESULTS FOR OTCB.90783

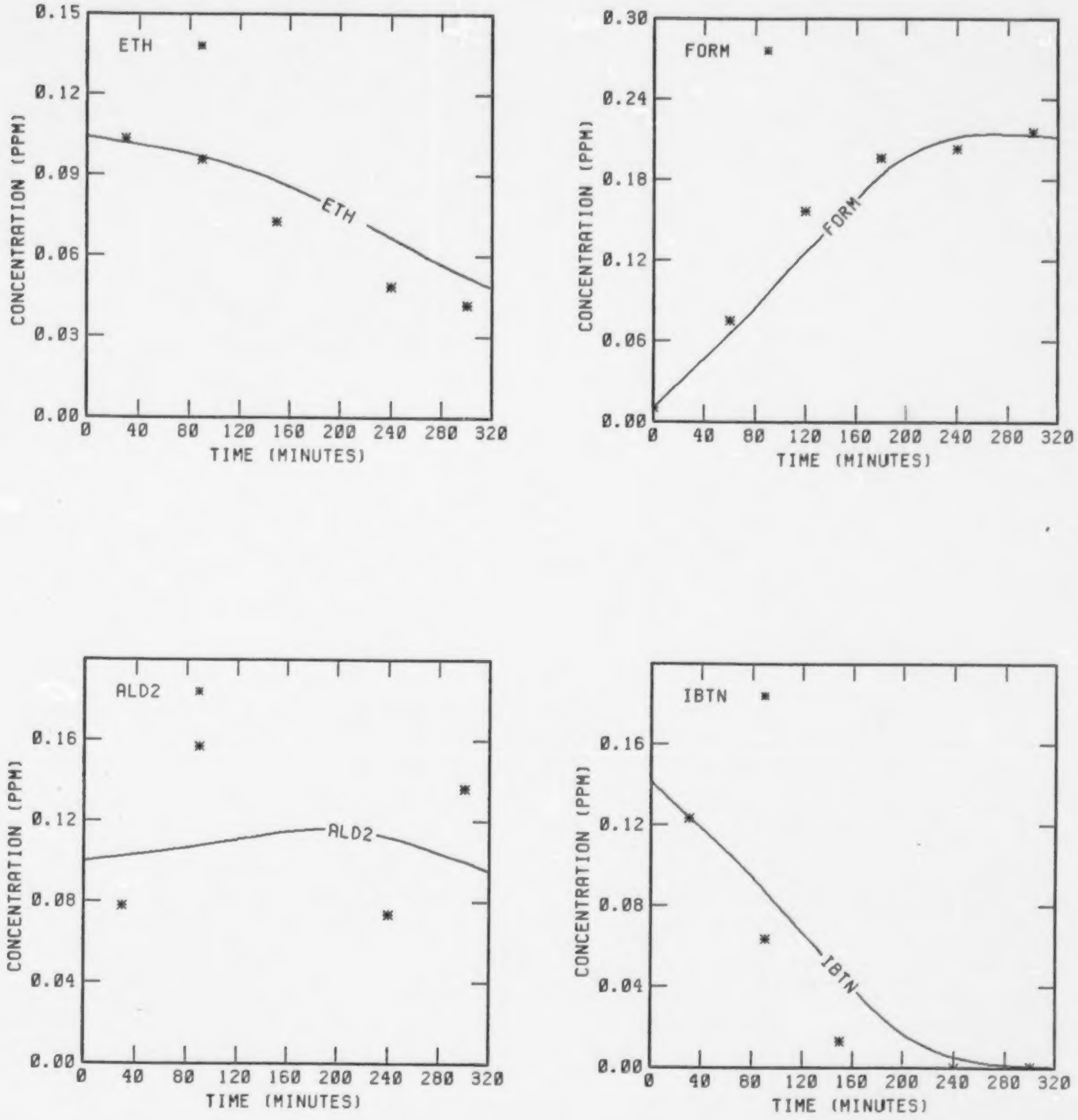


FIGURE C-24. SIMULATION RESULTS FOR OTCB.90783

(continued).

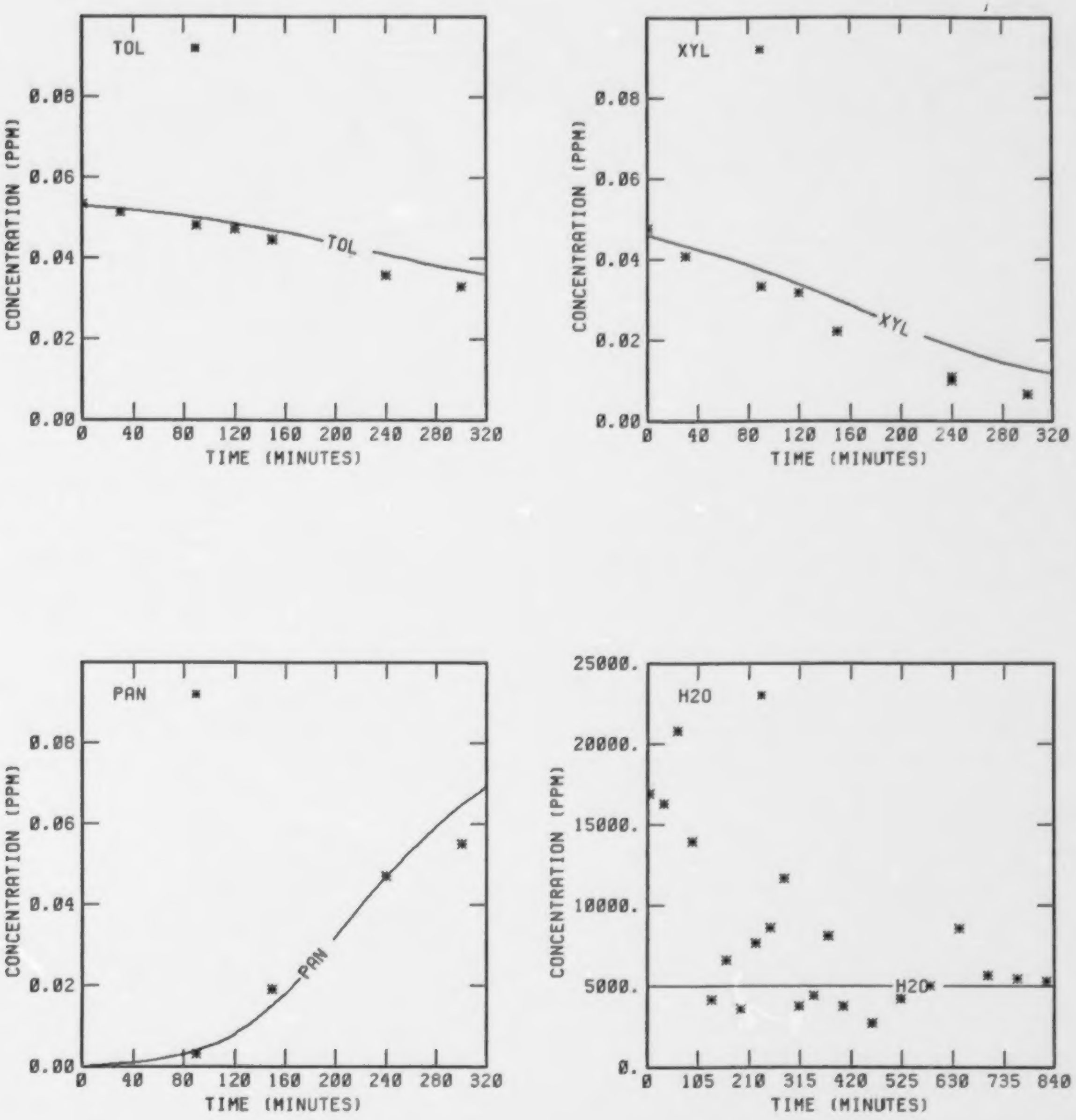


FIGURE C-24. SIMULATION RESULTS FOR
OTCB.90783

(continued).

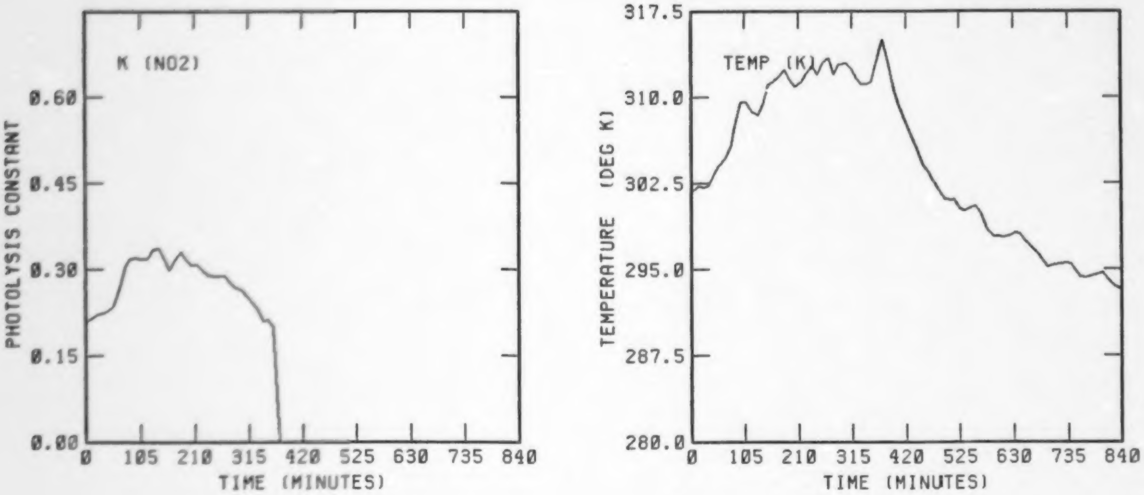


FIGURE **C-24.** SIMULATION RESULTS FOR
OTCB.90783

(concluded).

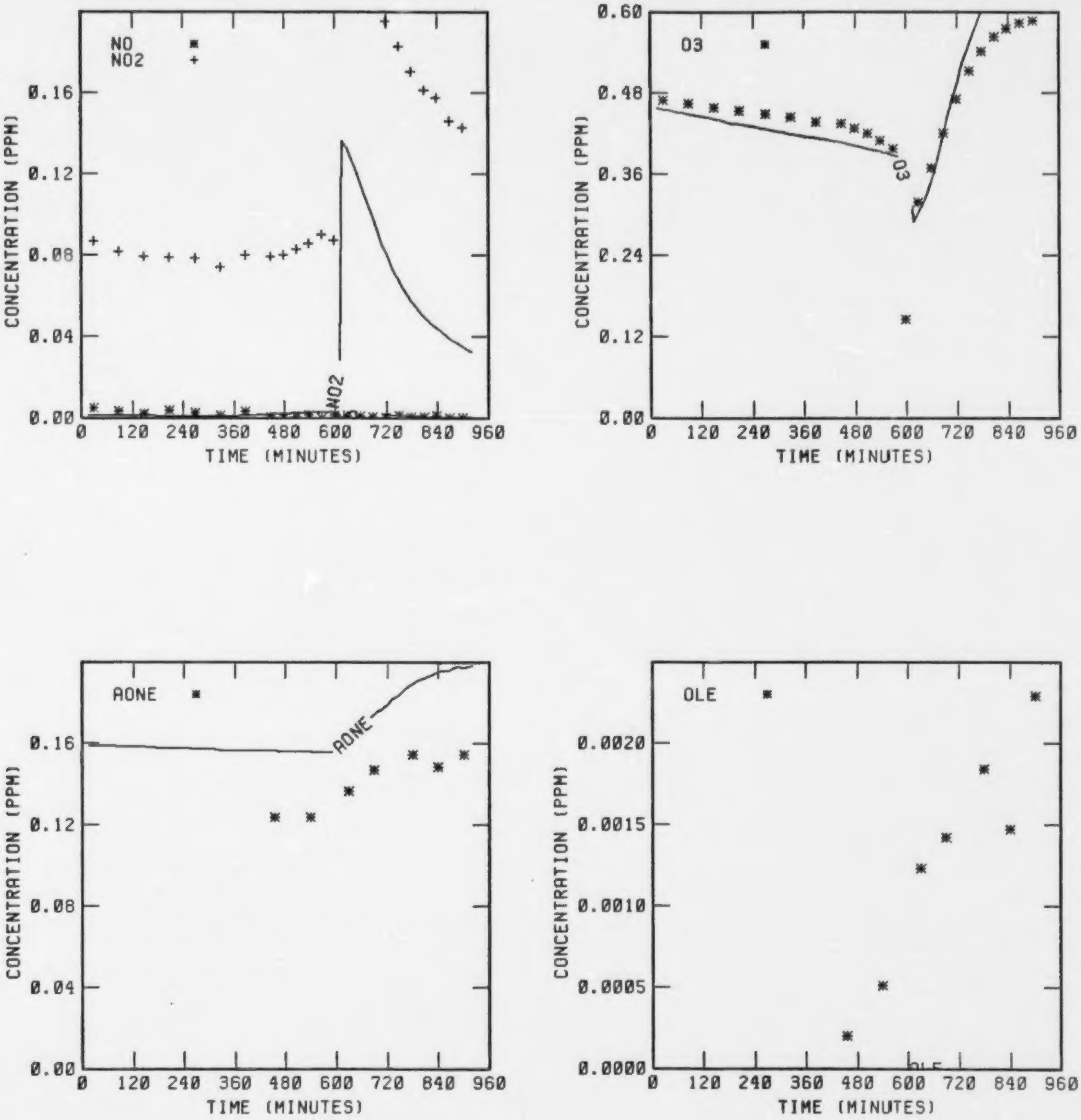


FIGURE C-25. SIMULATION RESULTS FOR OTCB.90883

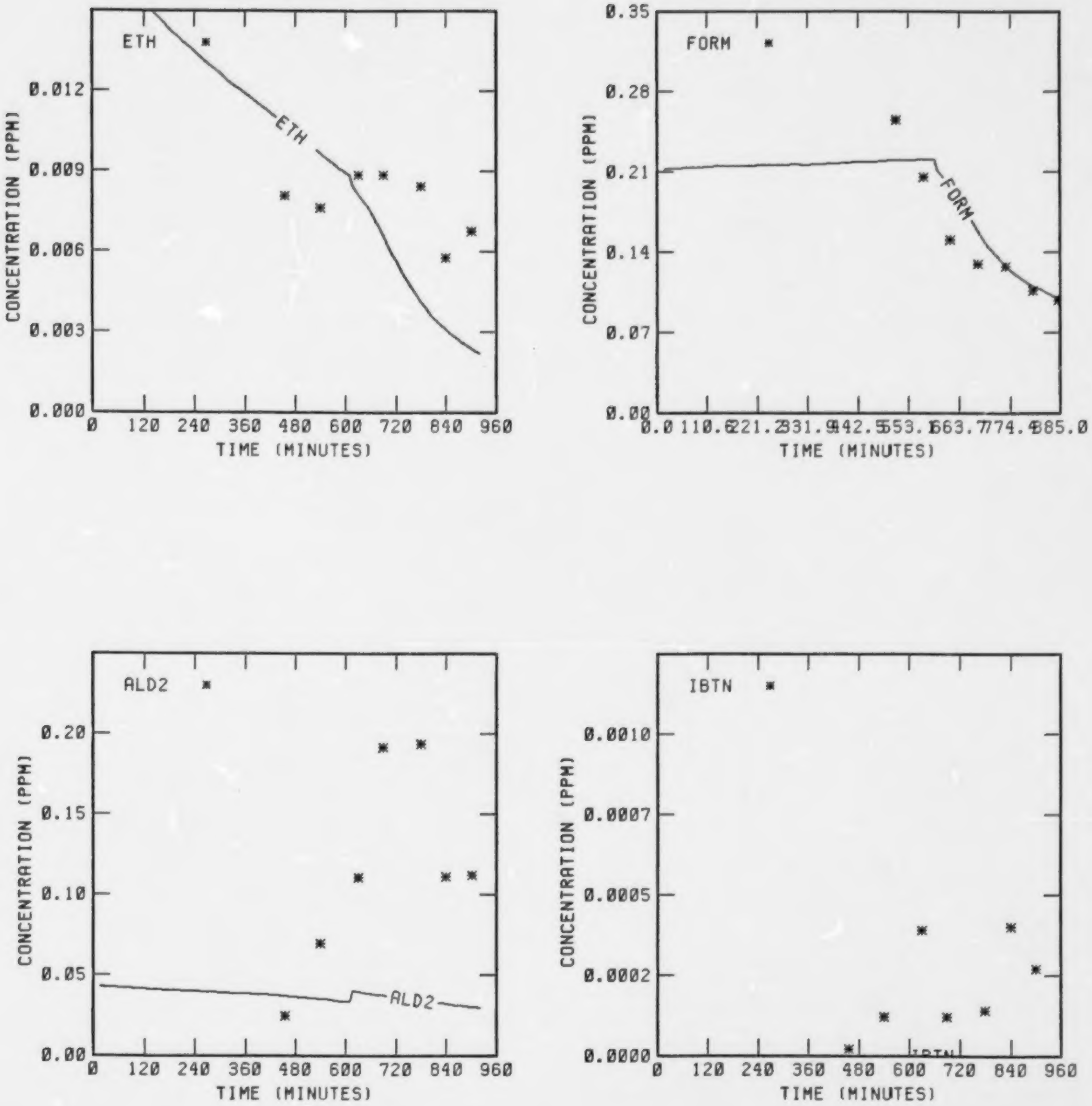


FIGURE C-25. SIMULATION RESULTS FOR
OTCB.90883
(continued).

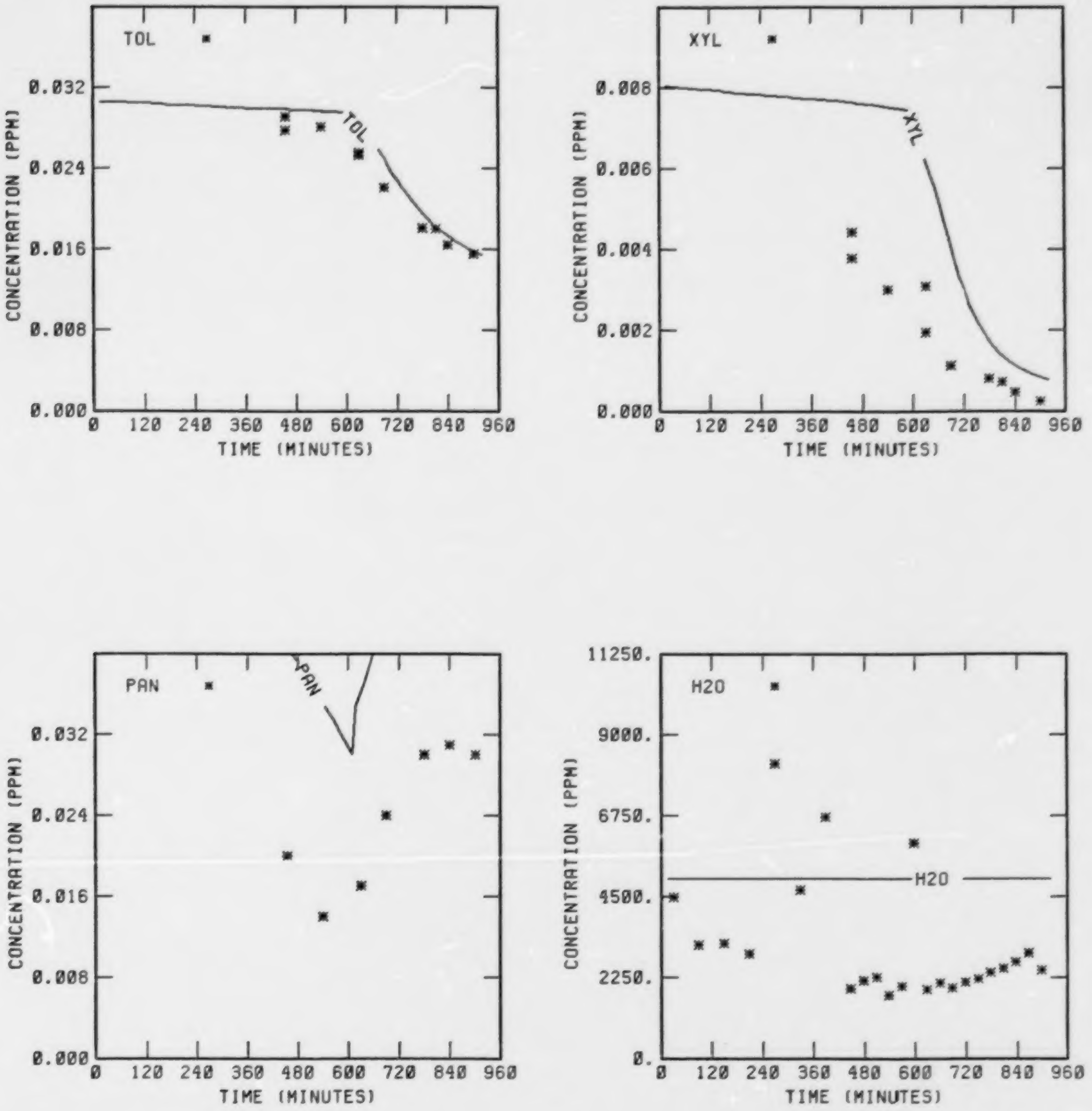


FIGURE C-25. SIMULATION RESULTS FOR OTCB.90883 (continued).

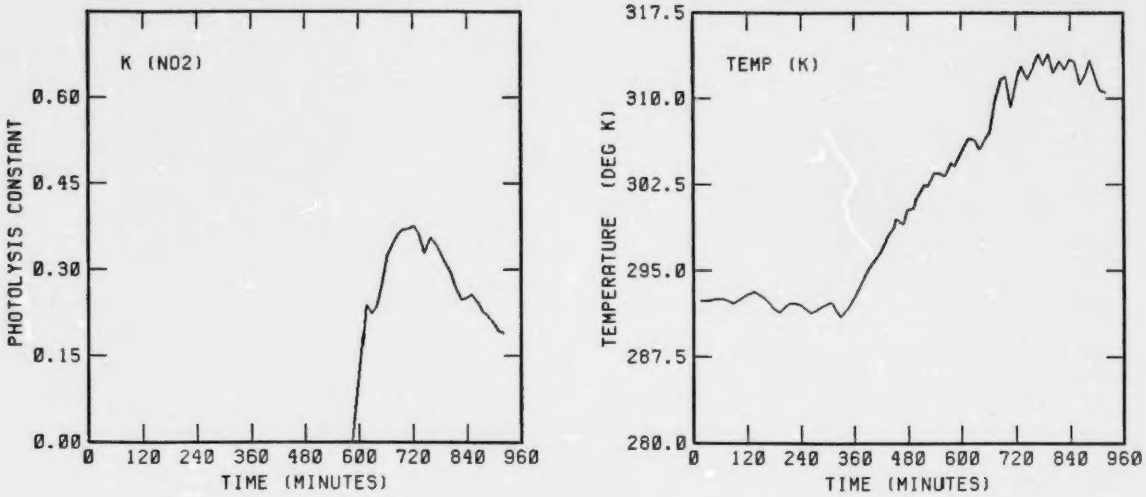


FIGURE C-25. SIMULATION RESULTS FOR
OTCB.90883
(concluded).

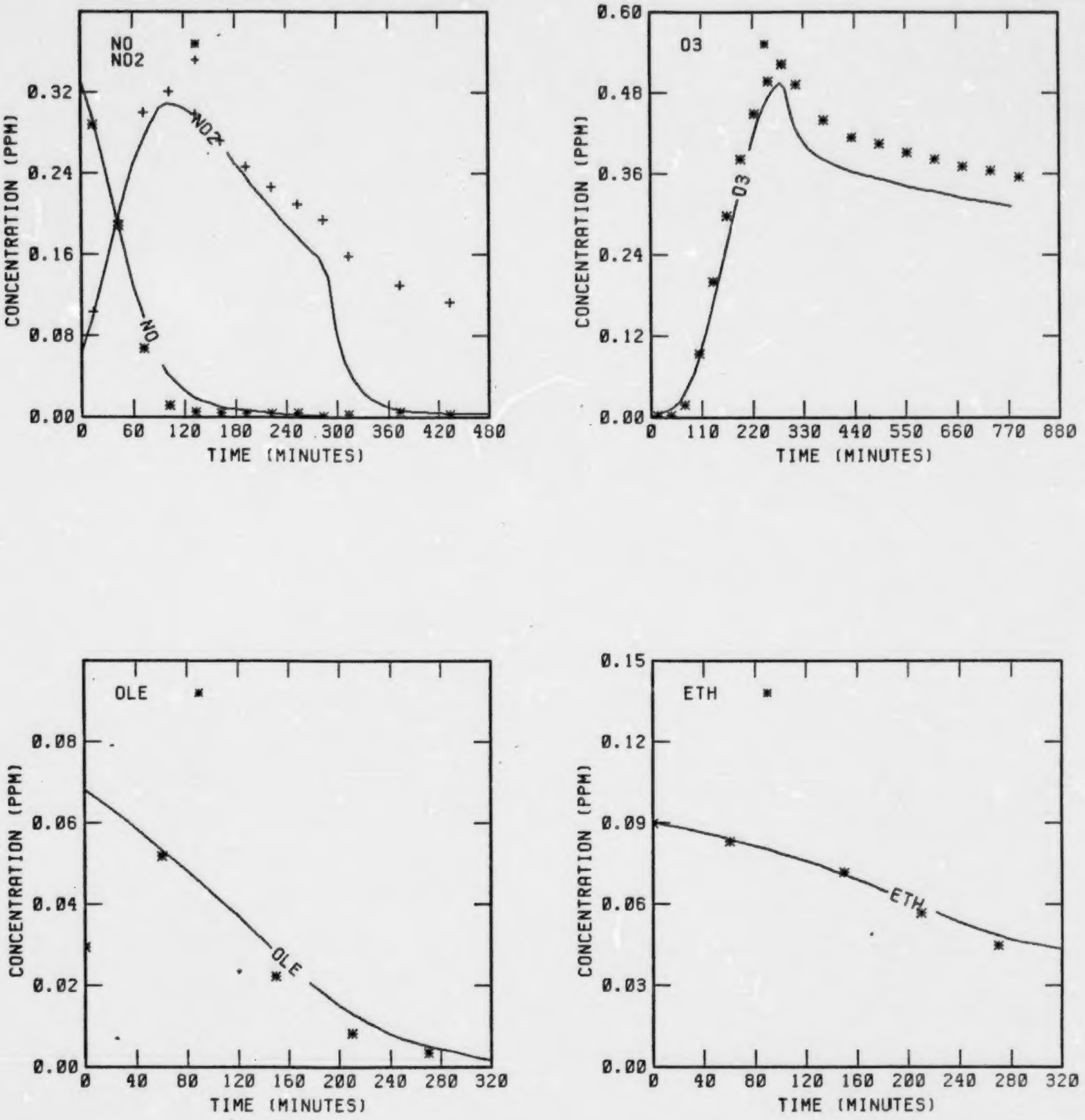


FIGURE C-26. SIMULATION RESULTS FOR
OTCB.92183

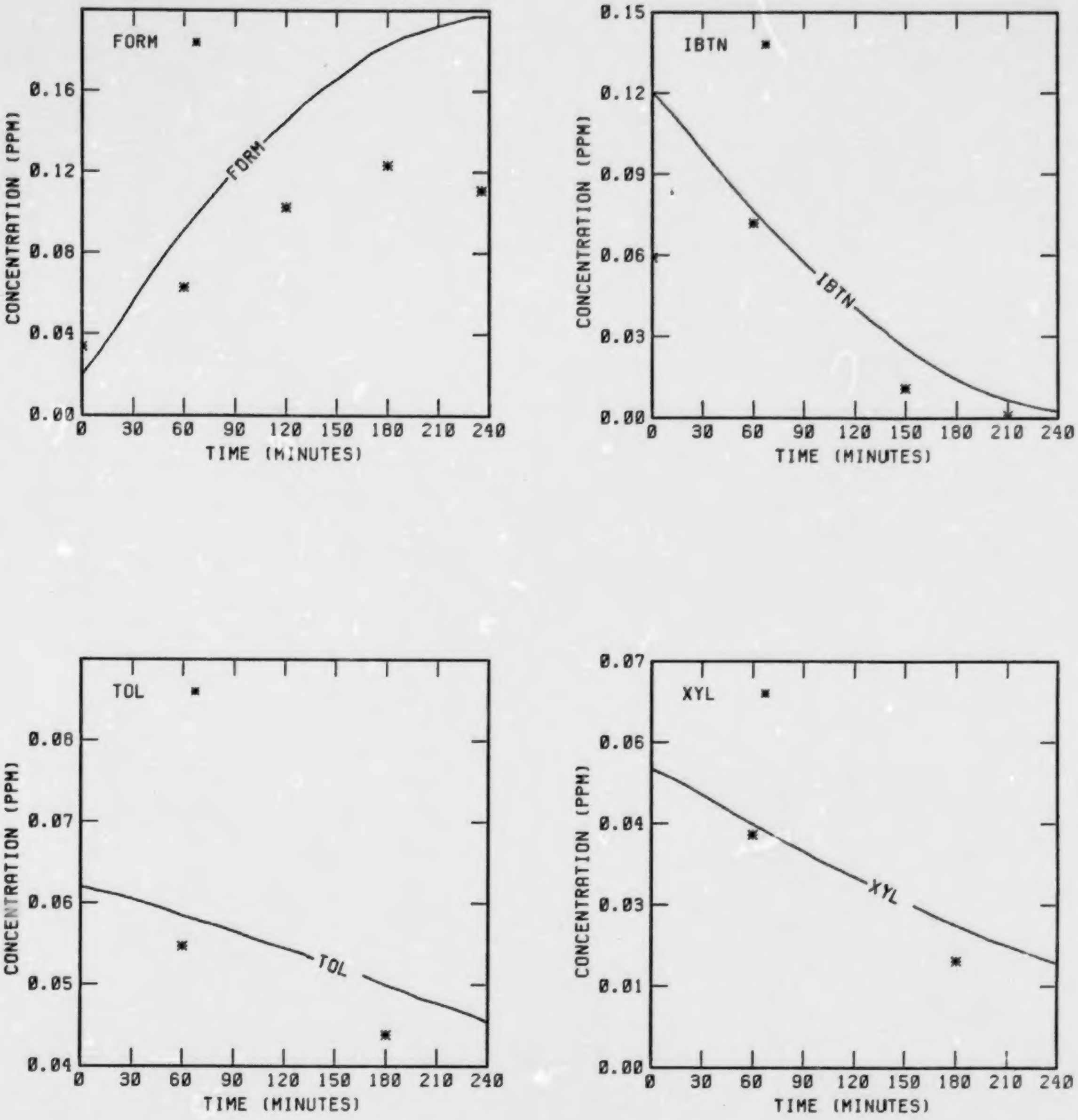


FIGURE C-26. SIMULATION RESULTS FOR
OTCB.92183

(continued).

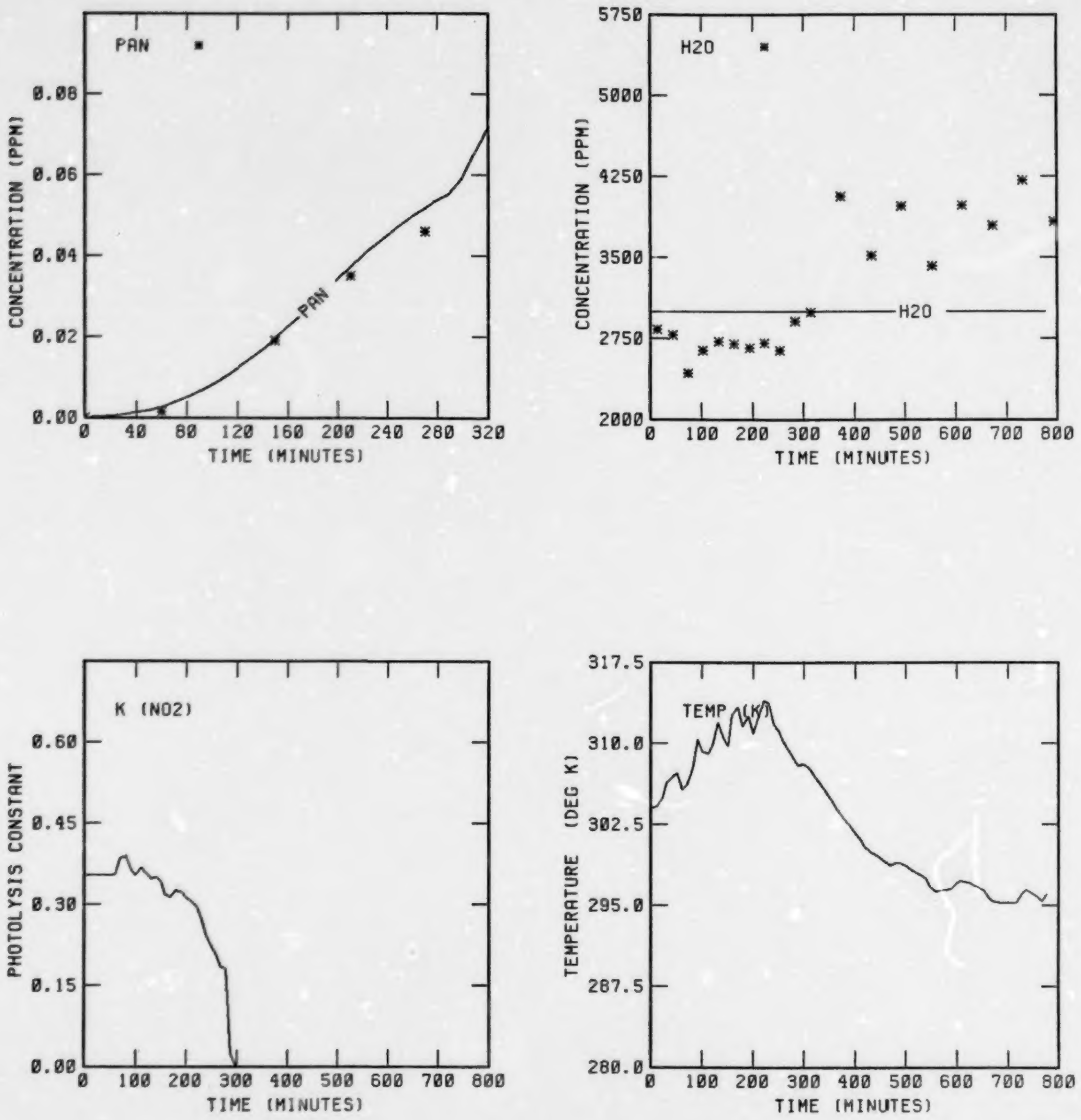


FIGURE C-26. SIMULATION RESULTS FOR
OTCB.92183

(concluded).

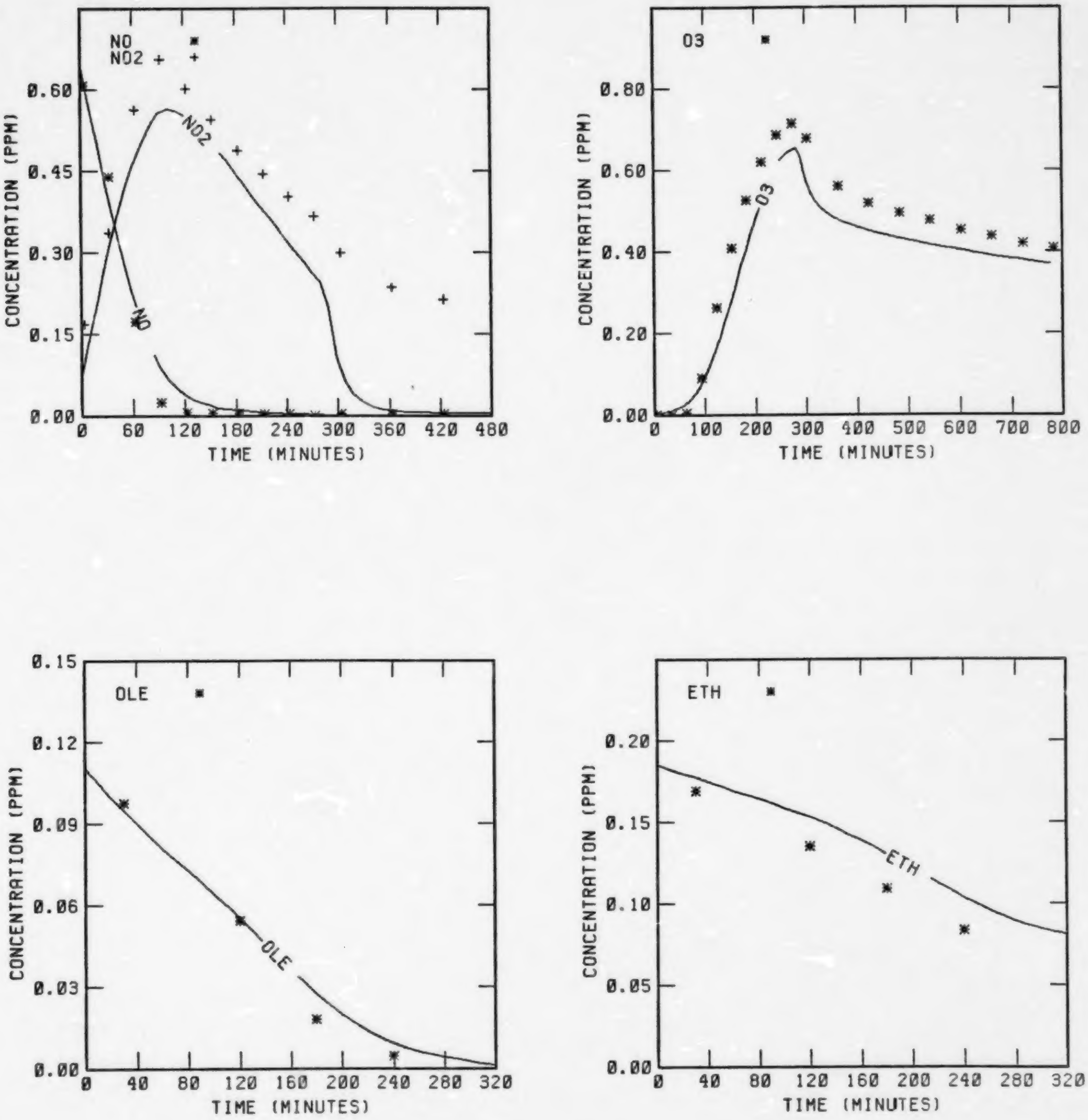


FIGURE C-27. SIMULATION RESULTS FOR OTCR.92183

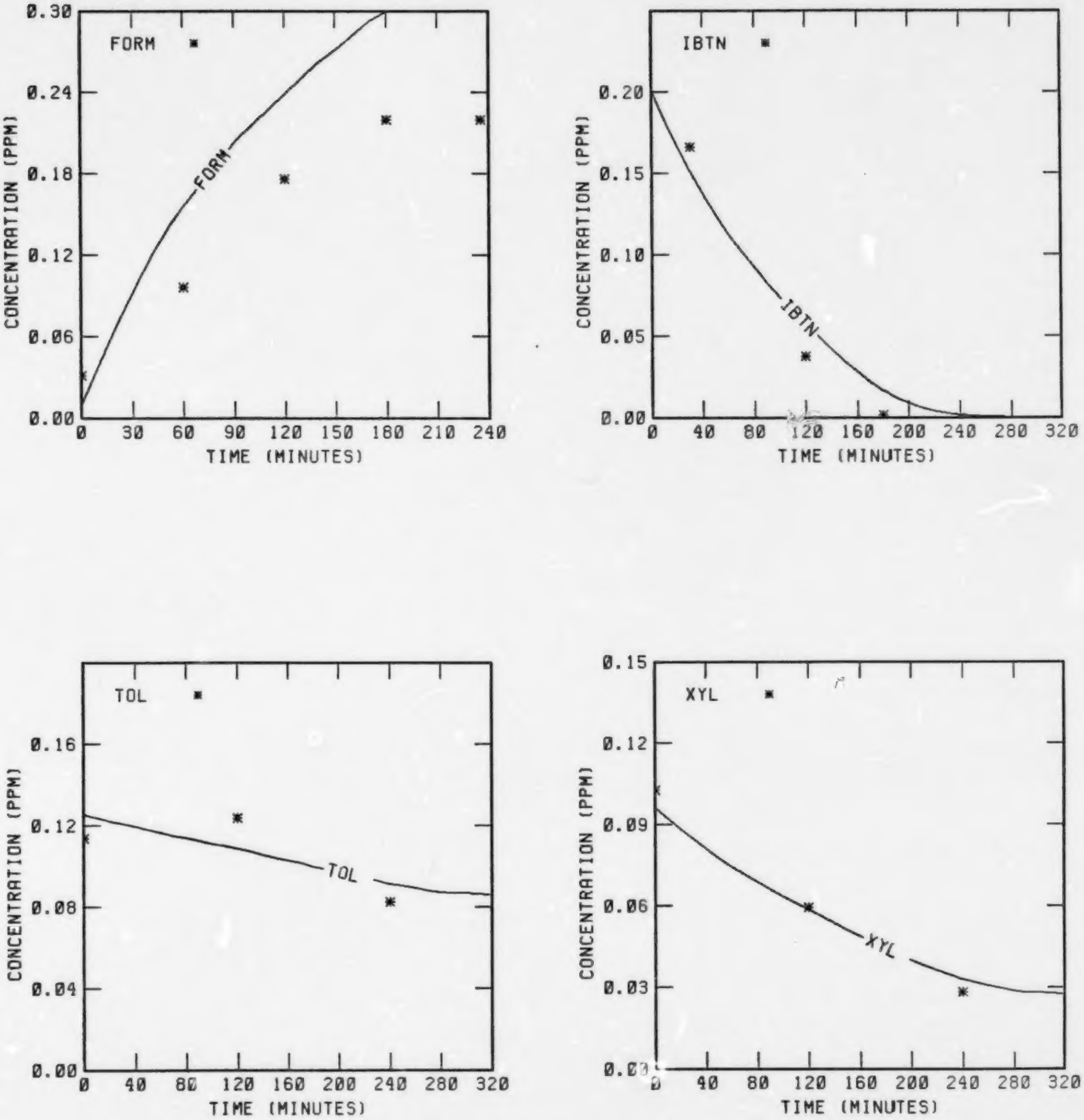


FIGURE C-27. SIMULATION RESULTS FOR
OTCR.92183
(continued).

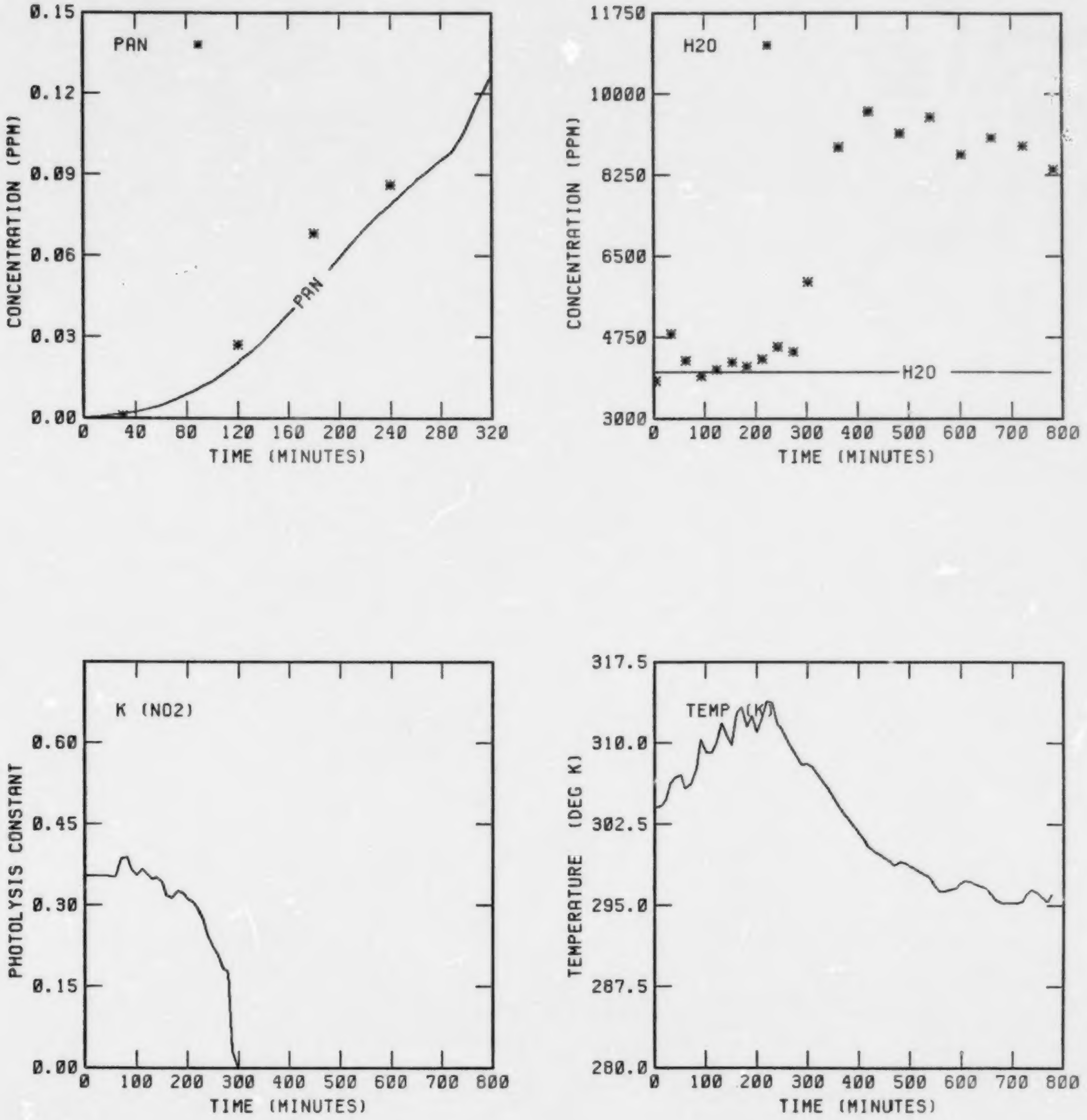


FIGURE C-27. SIMULATION RESULTS FOR
OTCR.92183

(concluded).

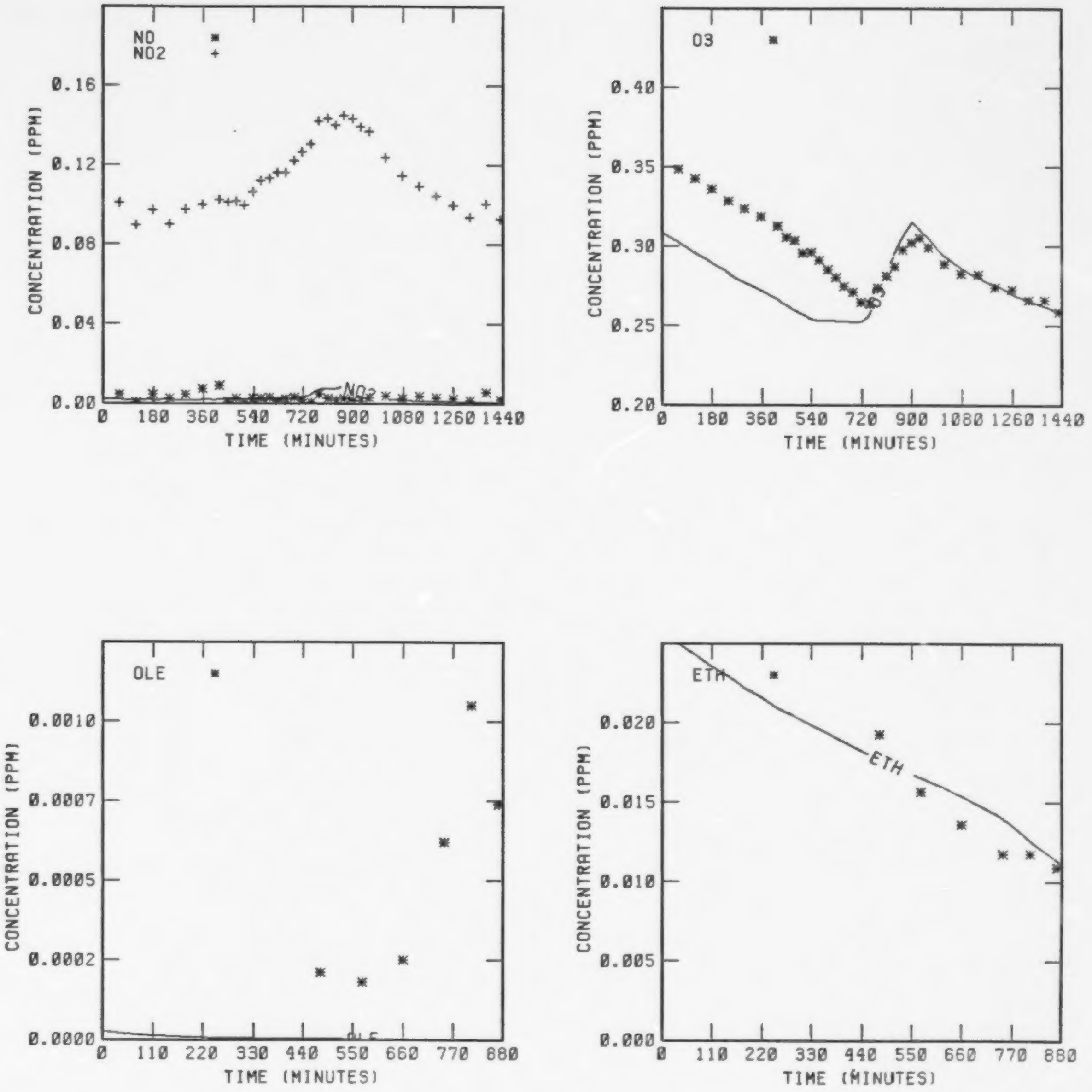


FIGURE C-28. SIMULATION RESULTS FOR
OTCB.92283

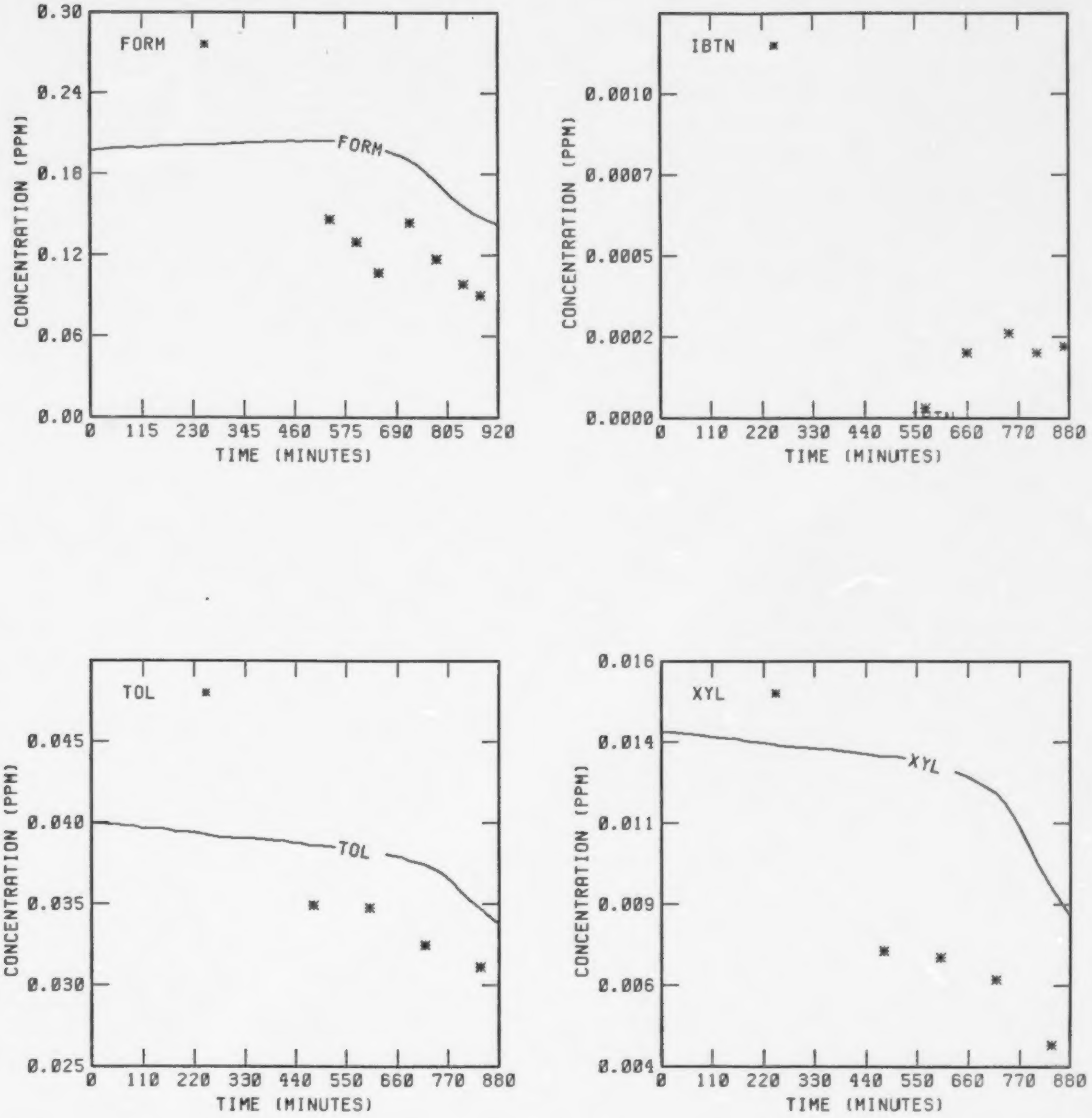


FIGURE C-28. SIMULATION RESULTS FOR
OTCB.92283

(continued).

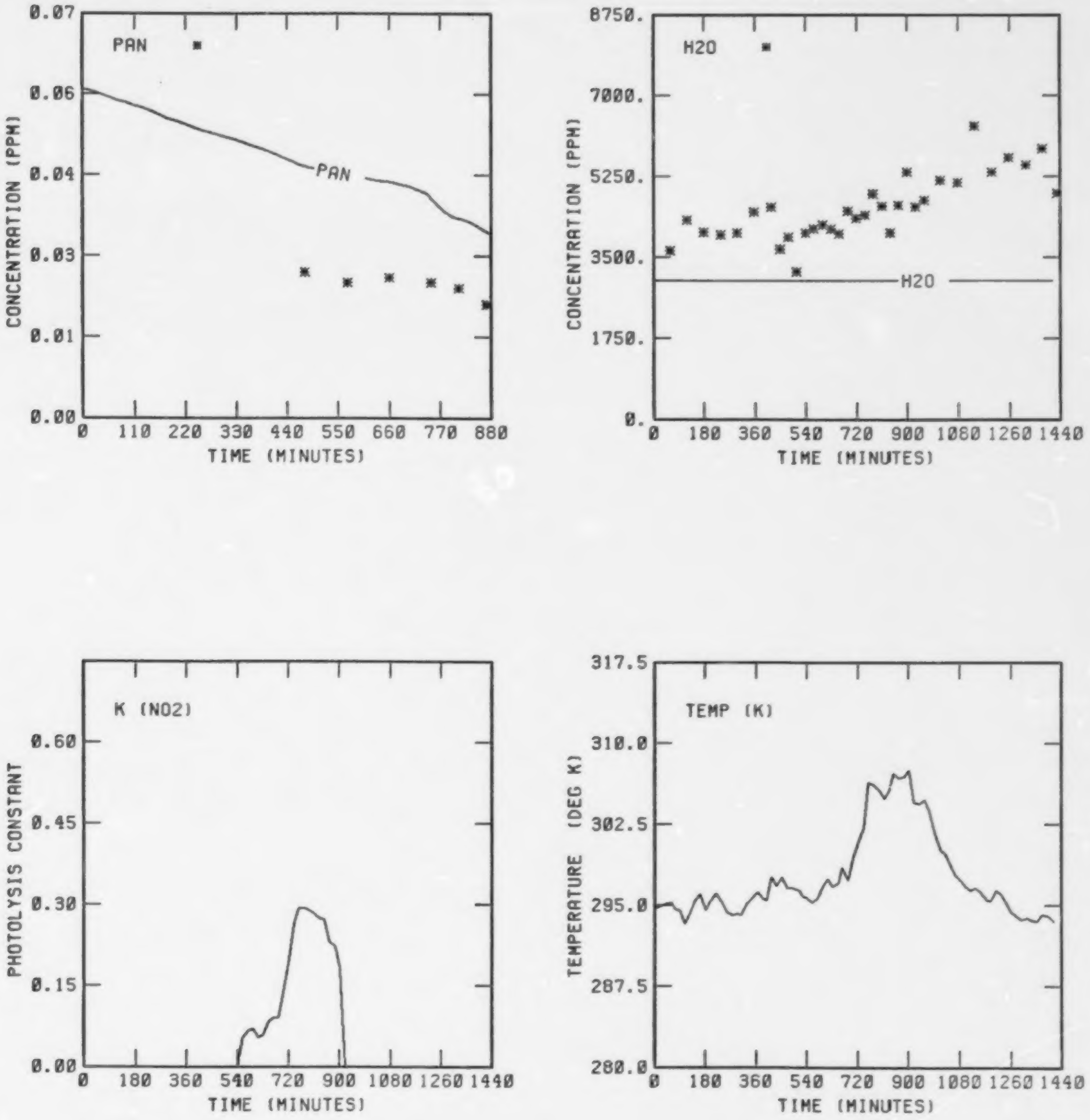


FIGURE C-28. SIMULATION RESULTS FOR OTCB.92283

(concluded).

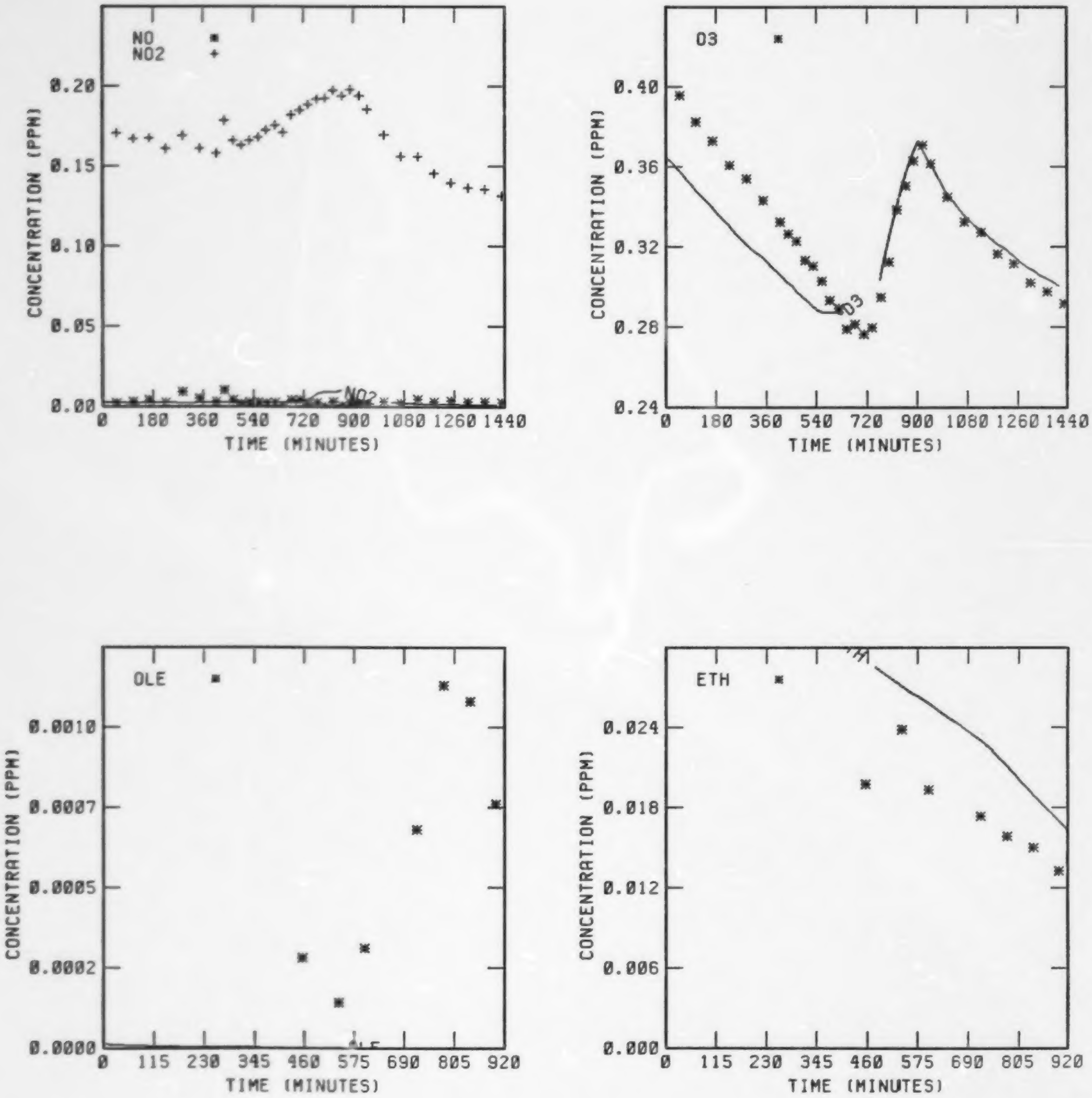


FIGURE C-29. SIMULATION RESULTS FOR
OTCR.92283

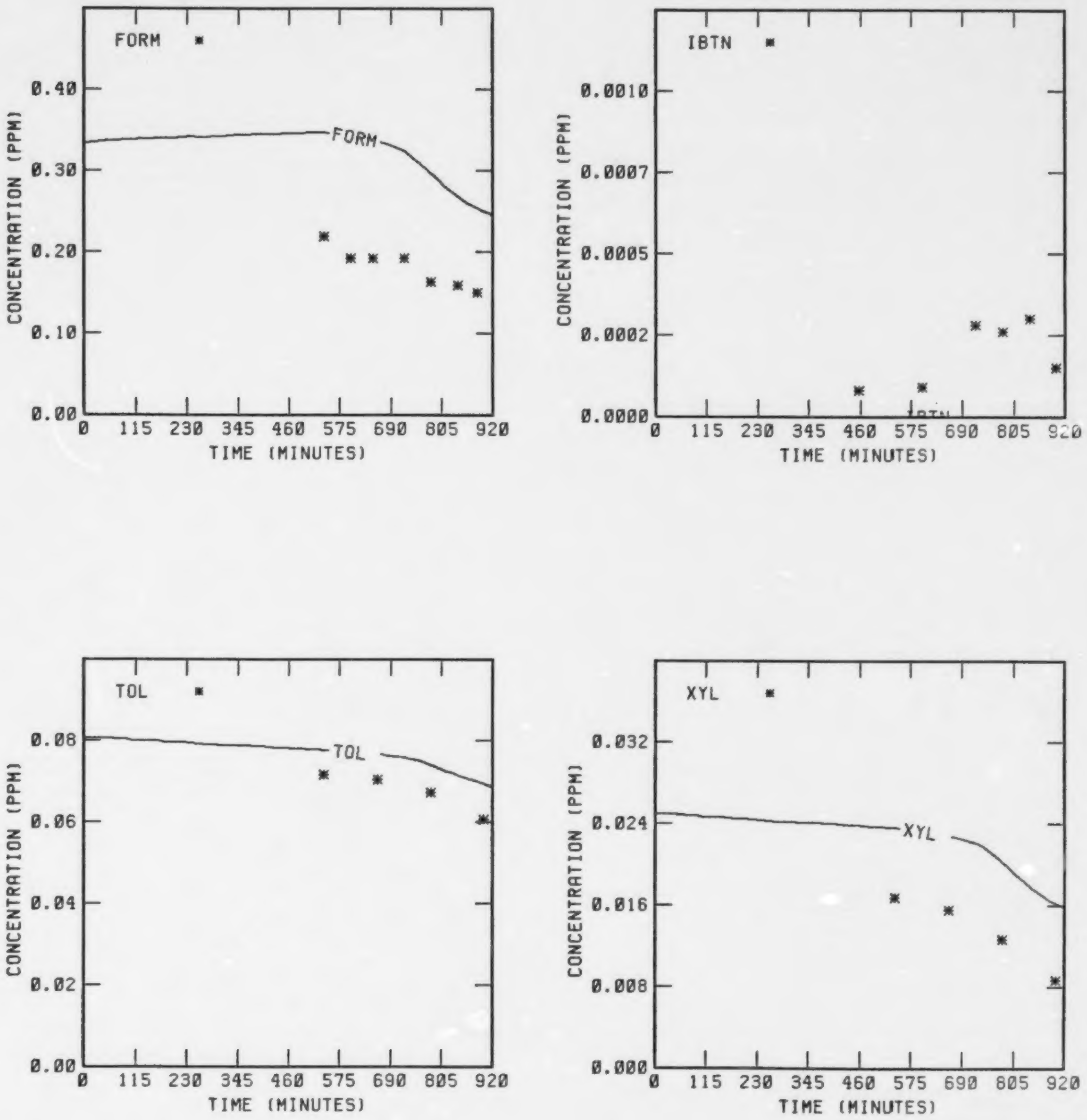


FIGURE C-29. SIMULATION RESULTS FOR
OTCR.92283
(continued).

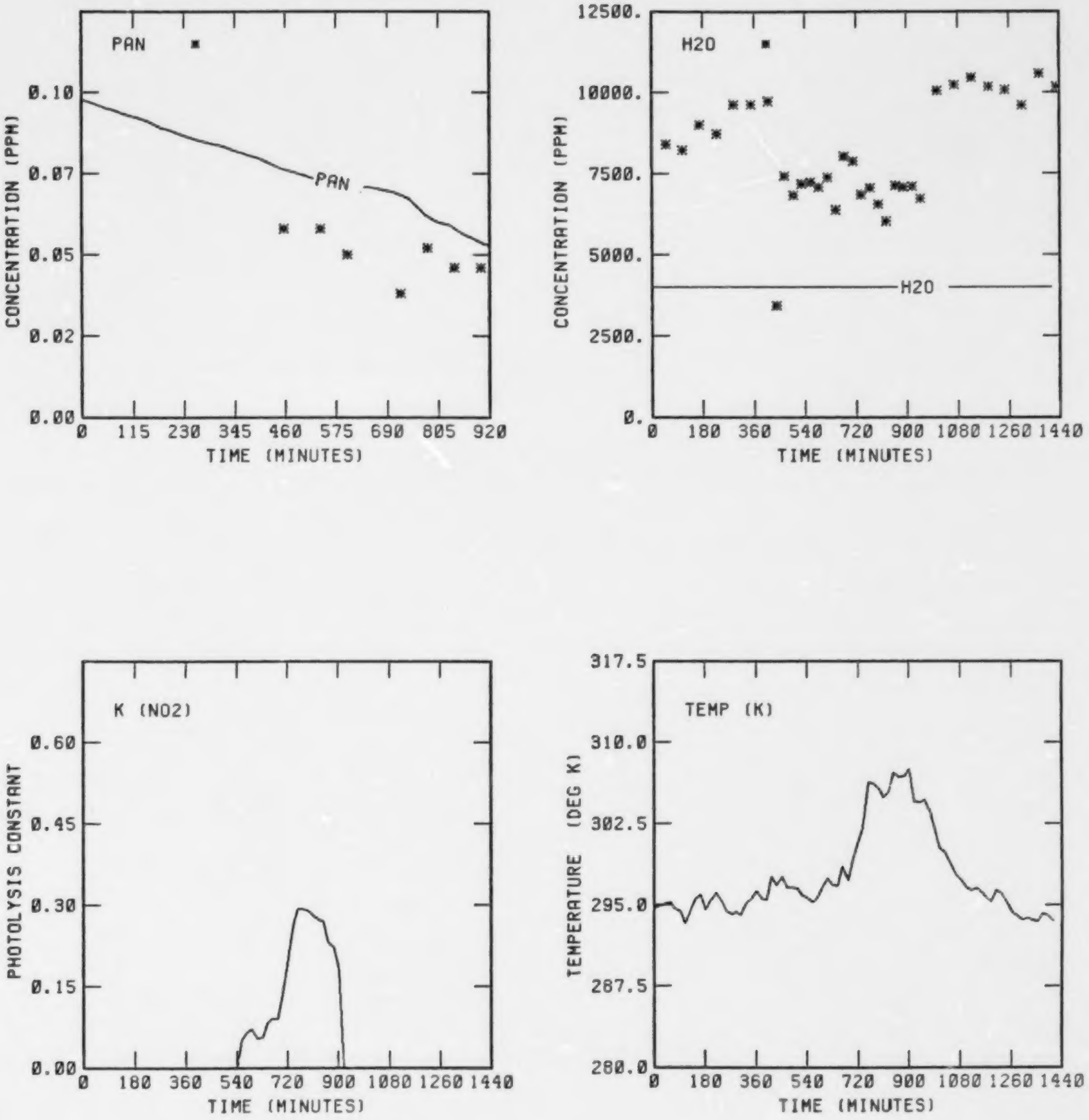


FIGURE C-29. SIMULATION RESULTS FOR OTCR.92283 (concluded).

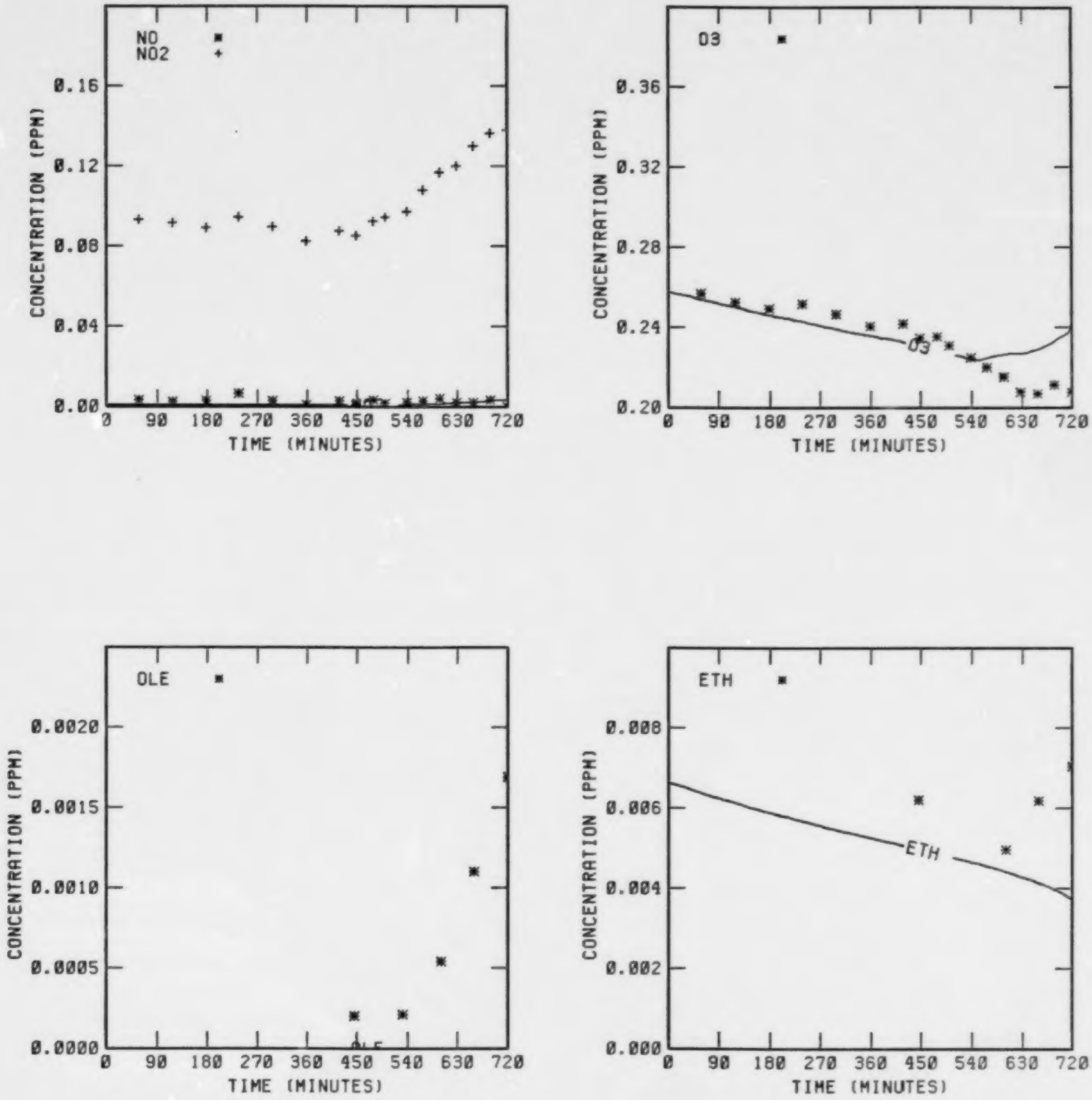


FIGURE C-30. SIMULATION RESULTS FOR
OTCB.92383

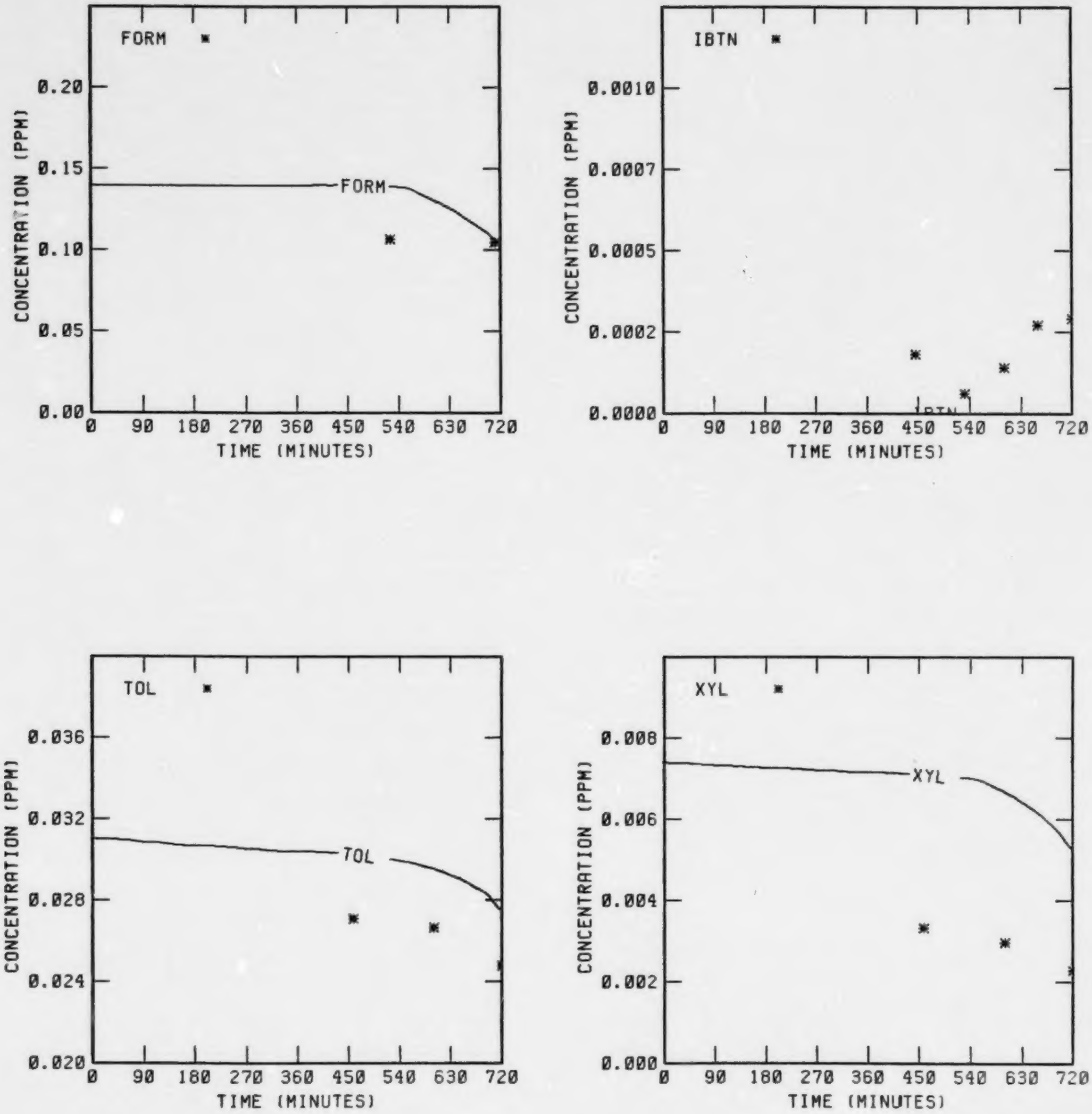


FIGURE C-30. SIMULATION RESULTS FOR OTCB.92383

(continued).

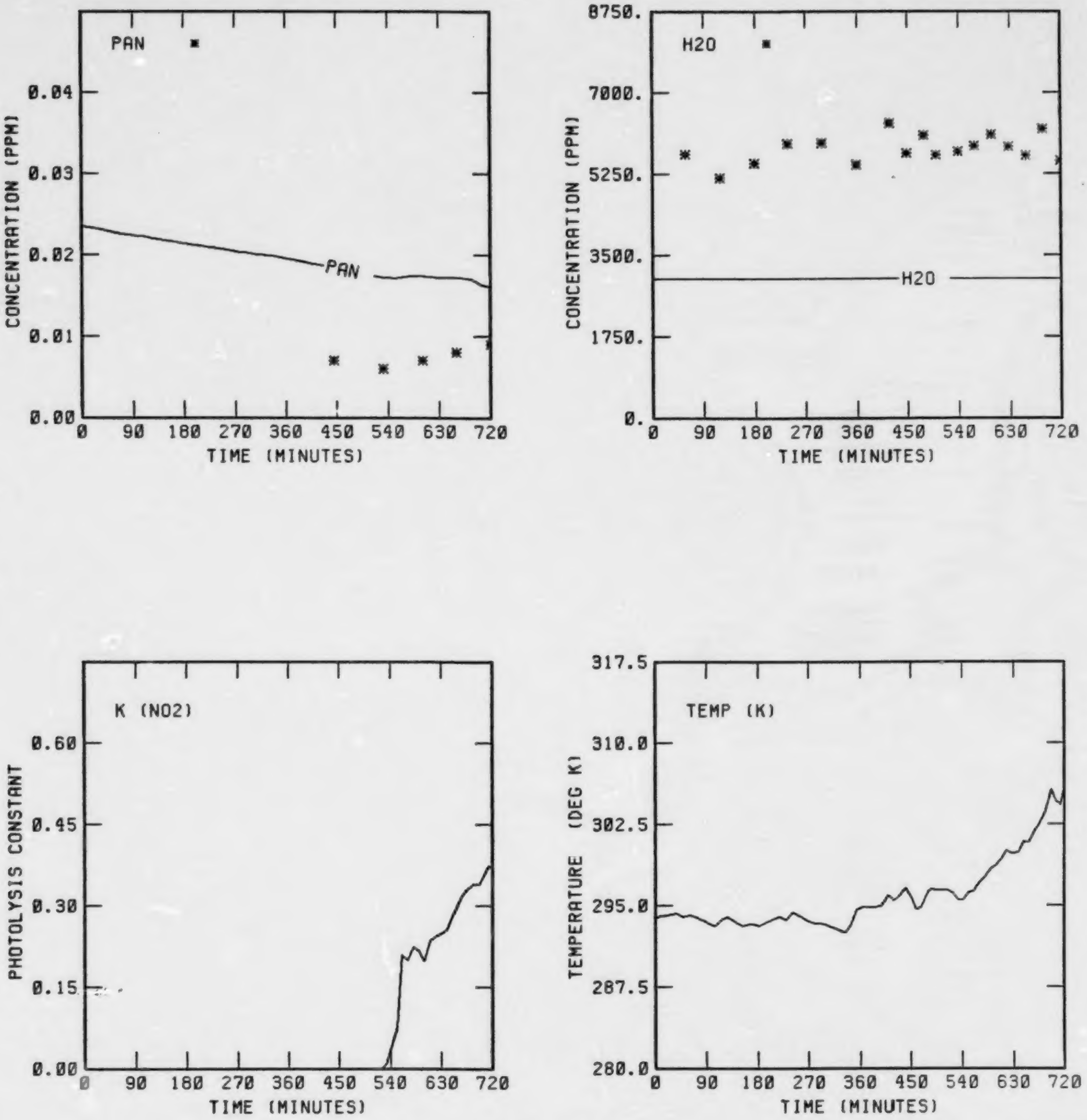


FIGURE C-30. SIMULATION RESULTS FOR
OTCB.92383

(concluded).

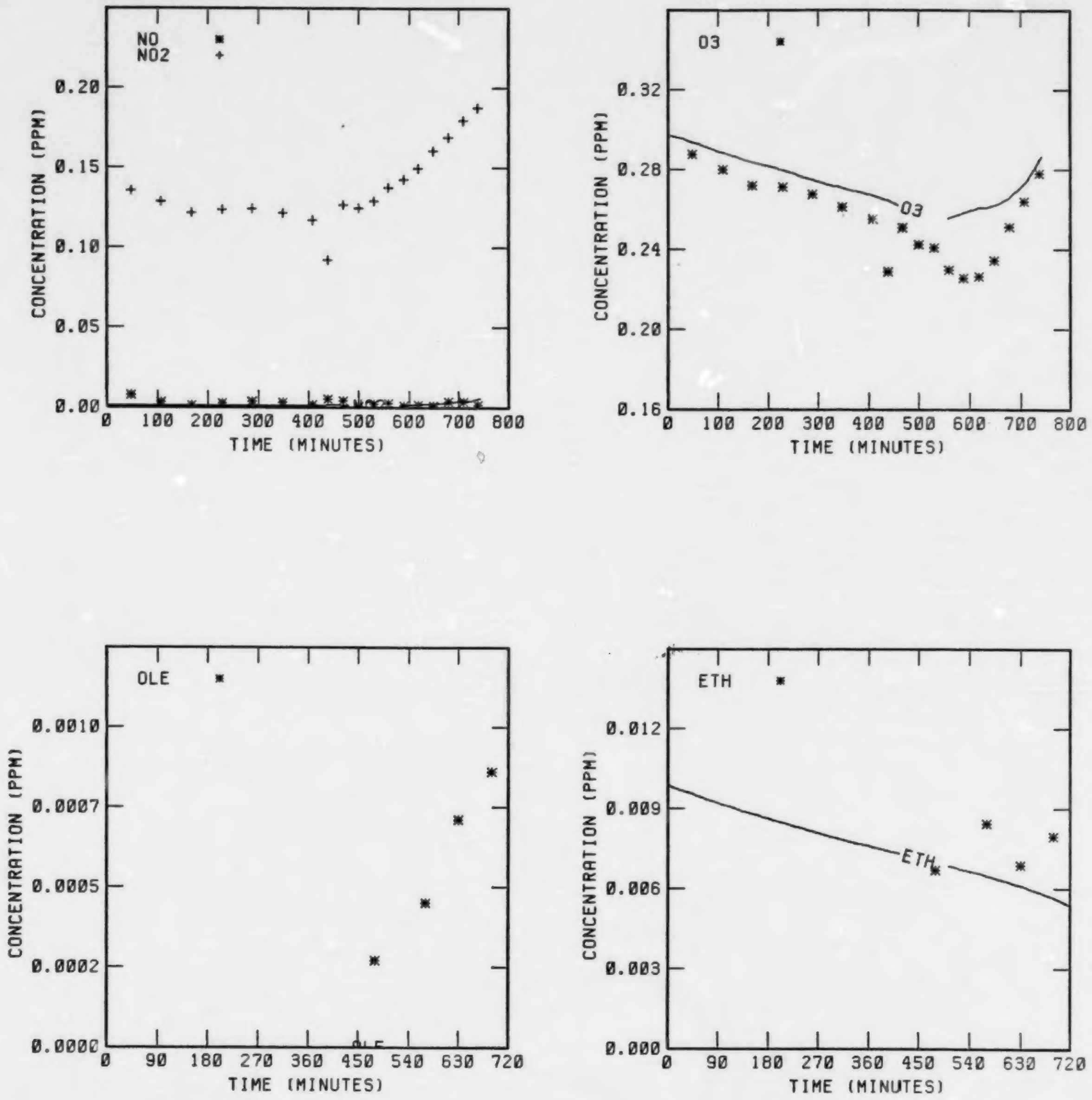


FIGURE C-31. SIMULATION RESULTS FOR OTCR.92383

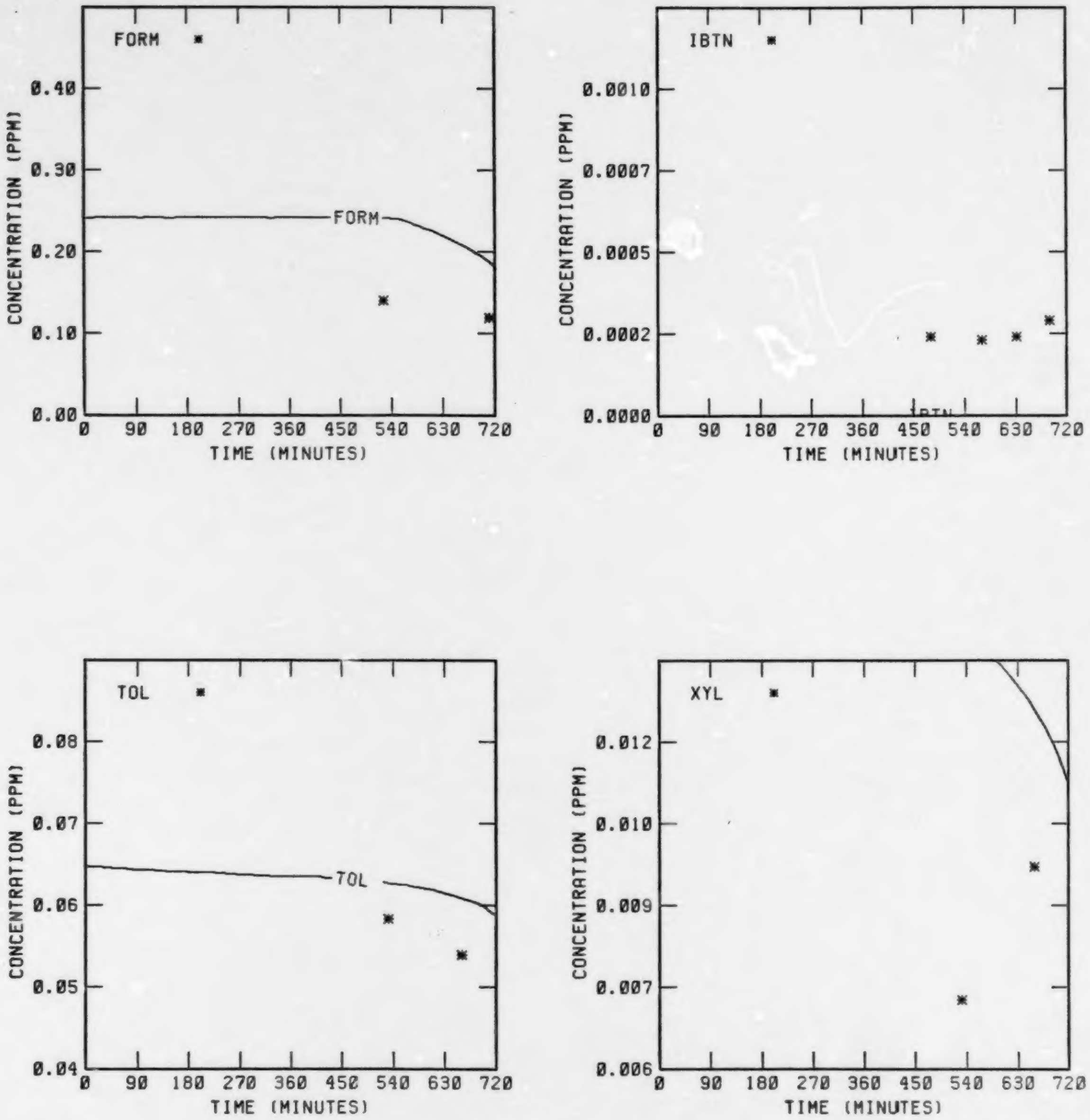


FIGURE C-31. SIMULATION RESULTS FOR
OTCR.92383

(continued).

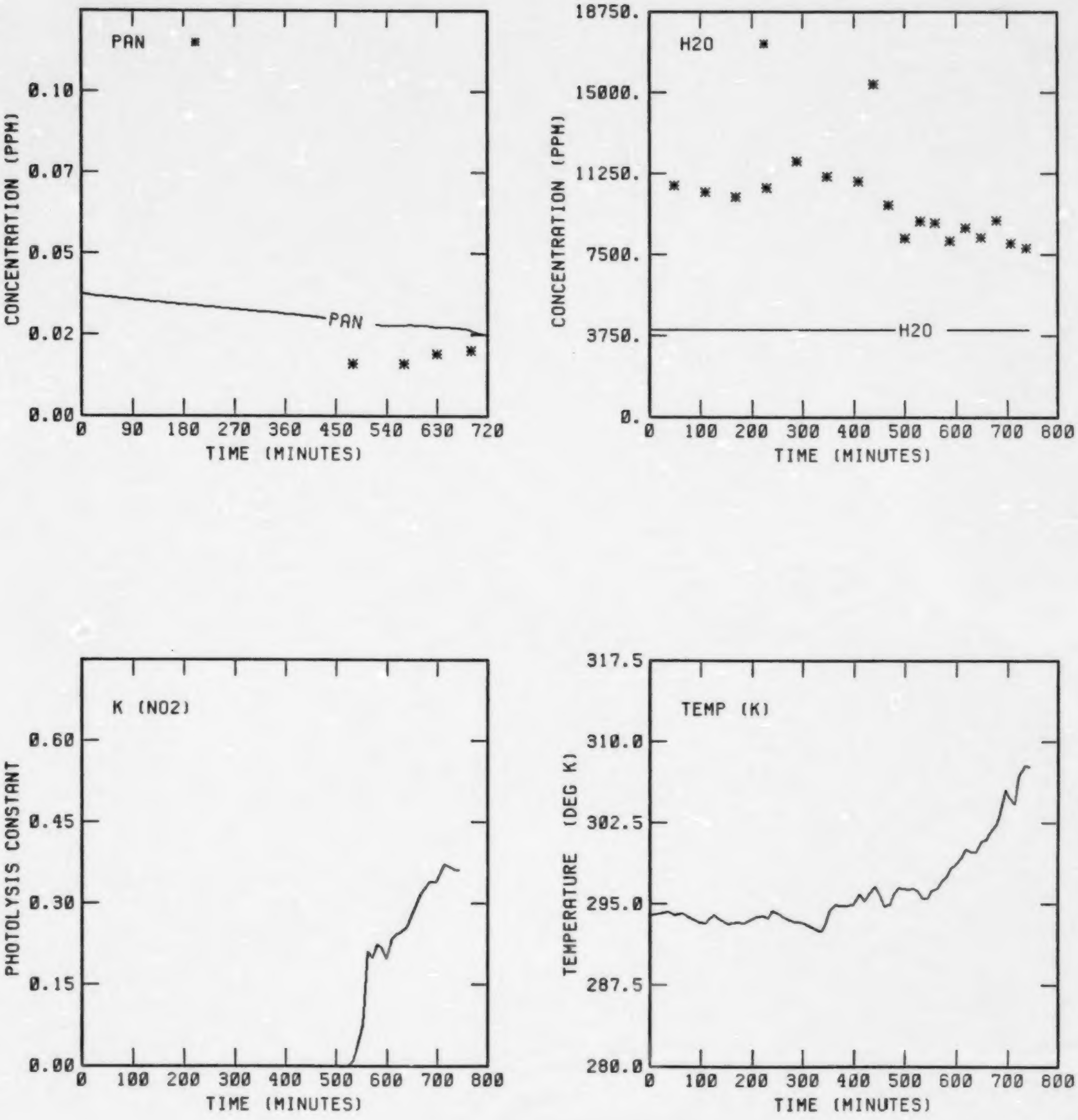


FIGURE C-31. SIMULATION RESULTS FOR OTCR.92383 (concluded).

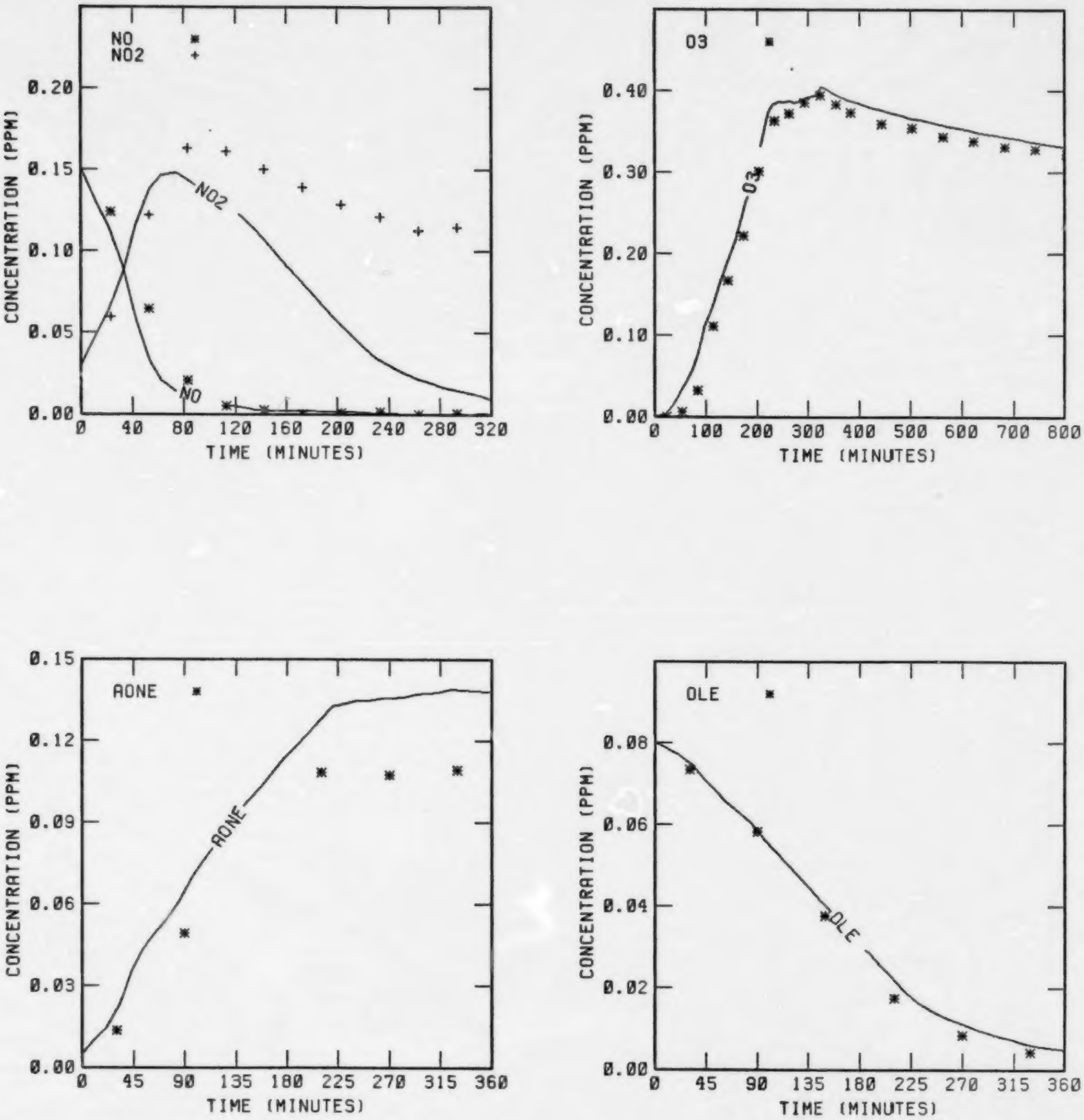


FIGURE C-32. SIMULATION RESULTS FOR OTCB.92883

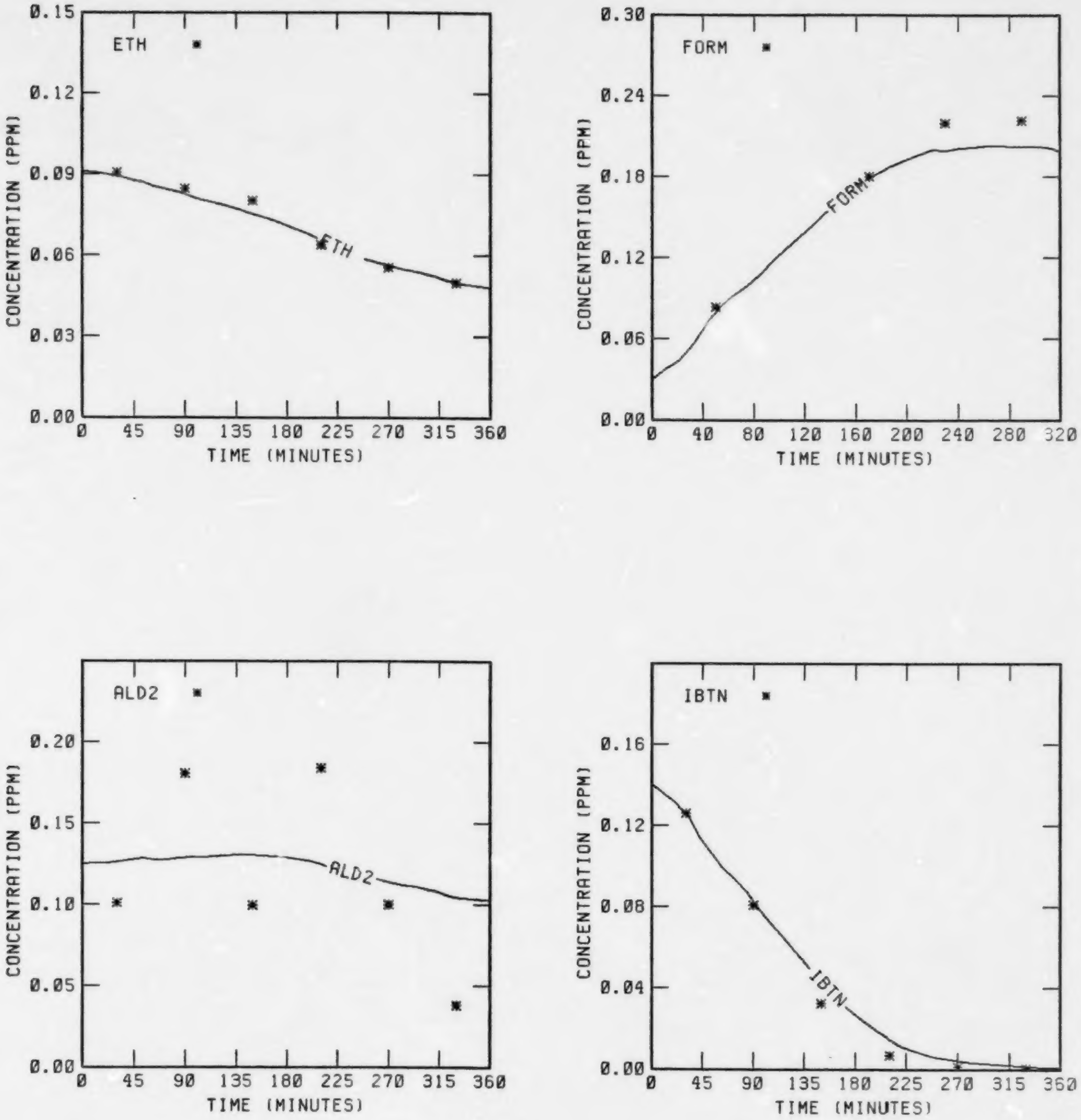


FIGURE C-32. SIMULATION RESULTS FOR
OTCB.92883

(continued).

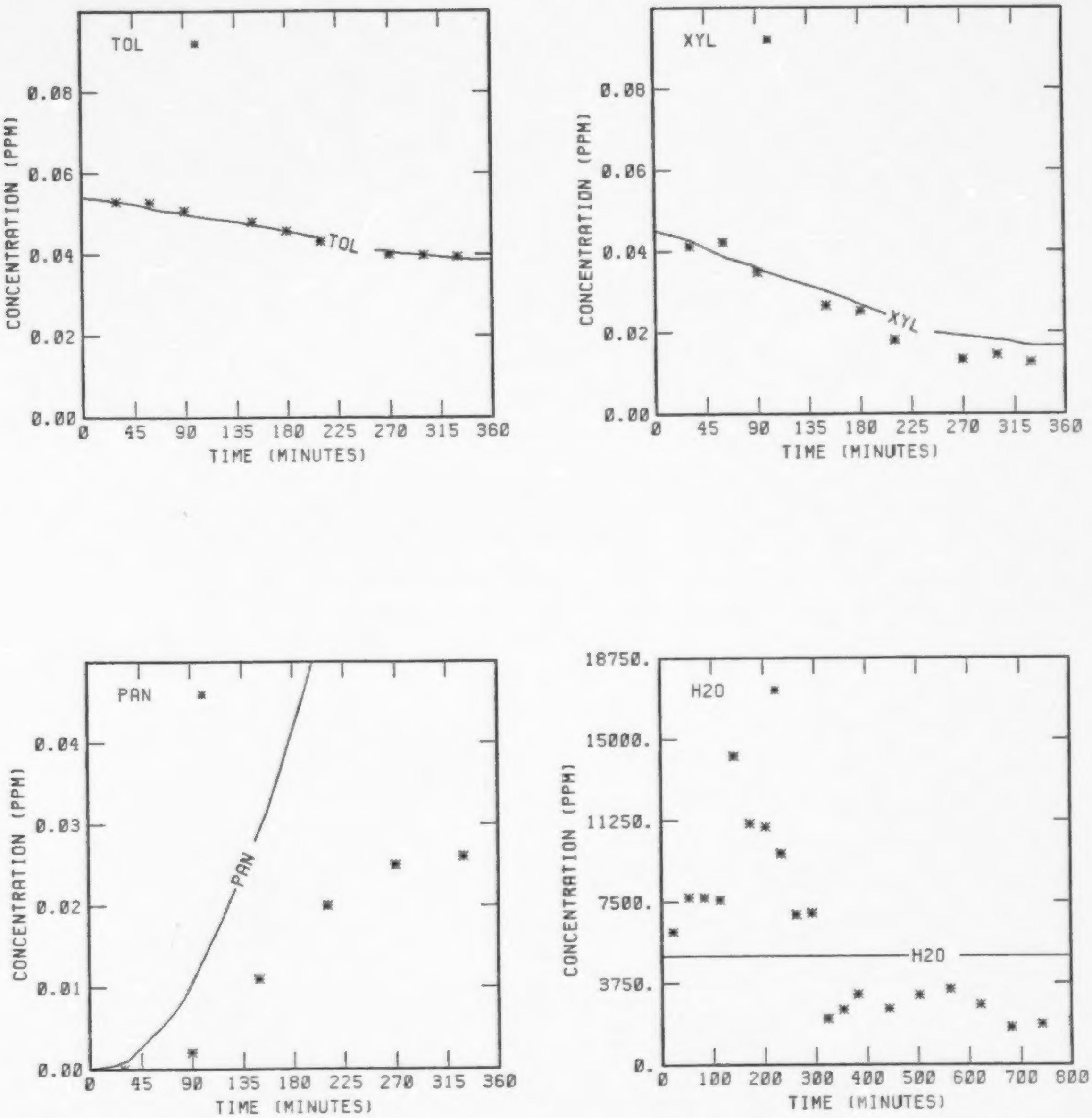


FIGURE C-32. SIMULATION RESULTS FOR
OTCB.92883

(continued).

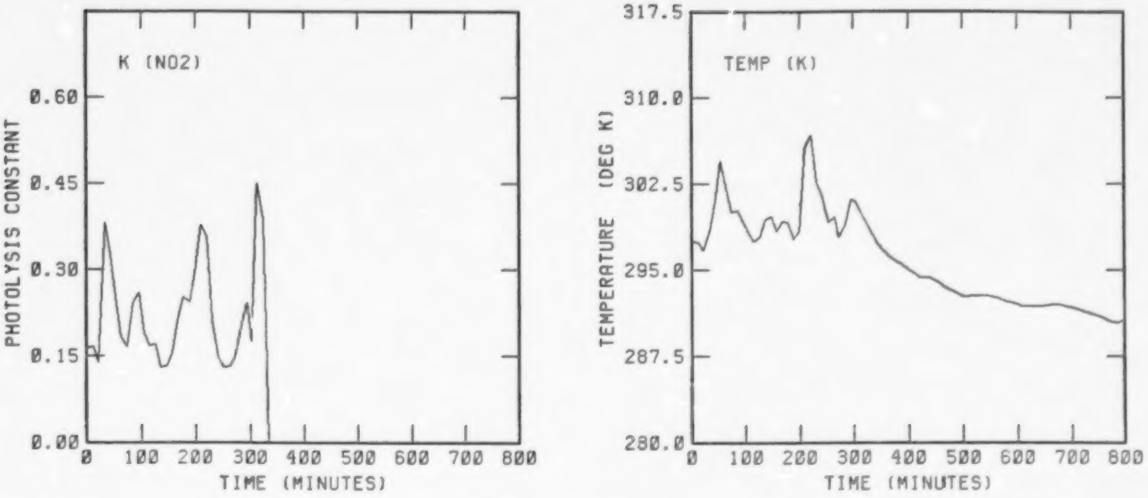


FIGURE C-32. SIMULATION RESULTS FOR
OTCB.92883
(concluded).

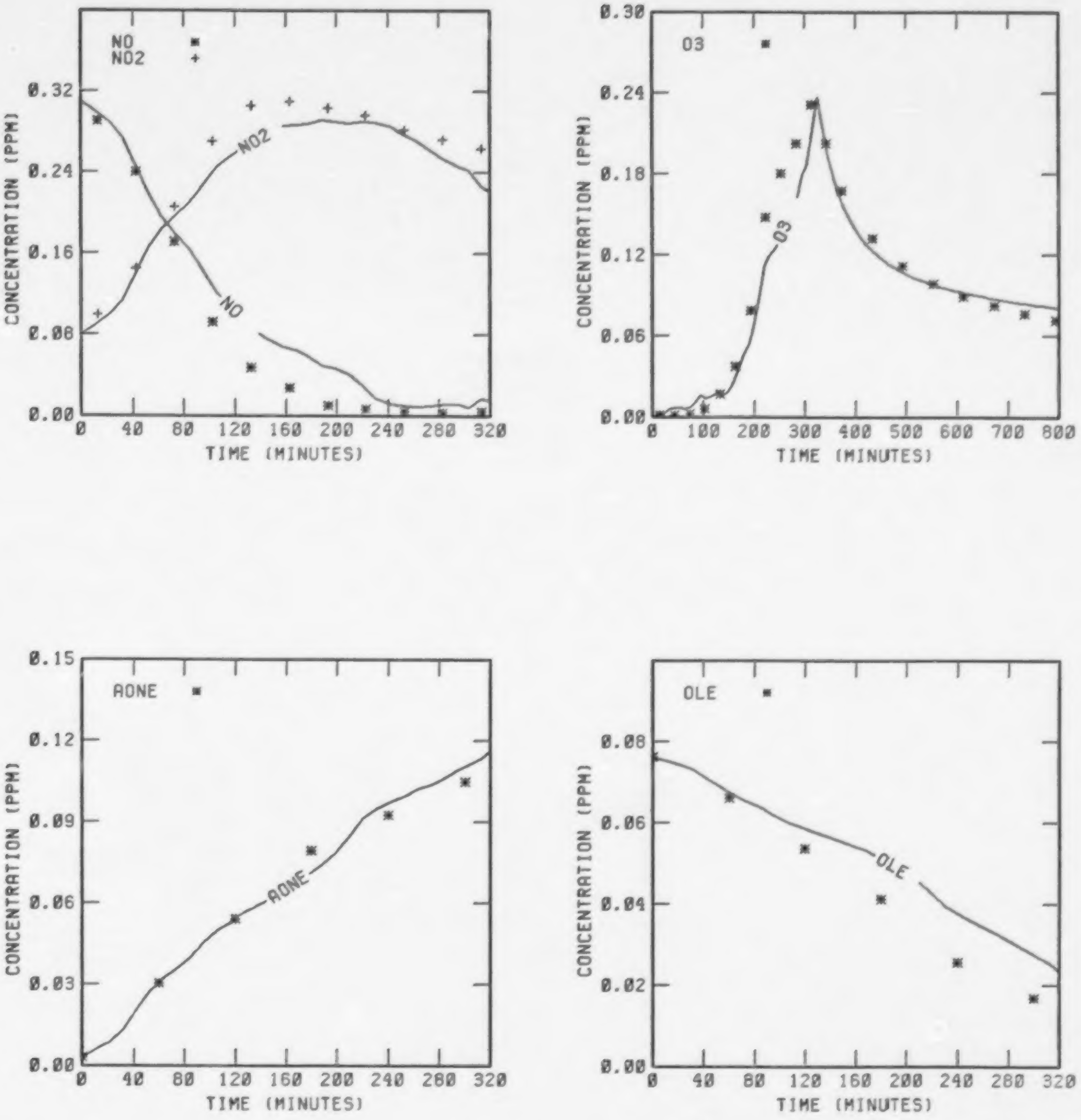


FIGURE C-33. SIMULATION RESULTS FOR
OTCR.92883

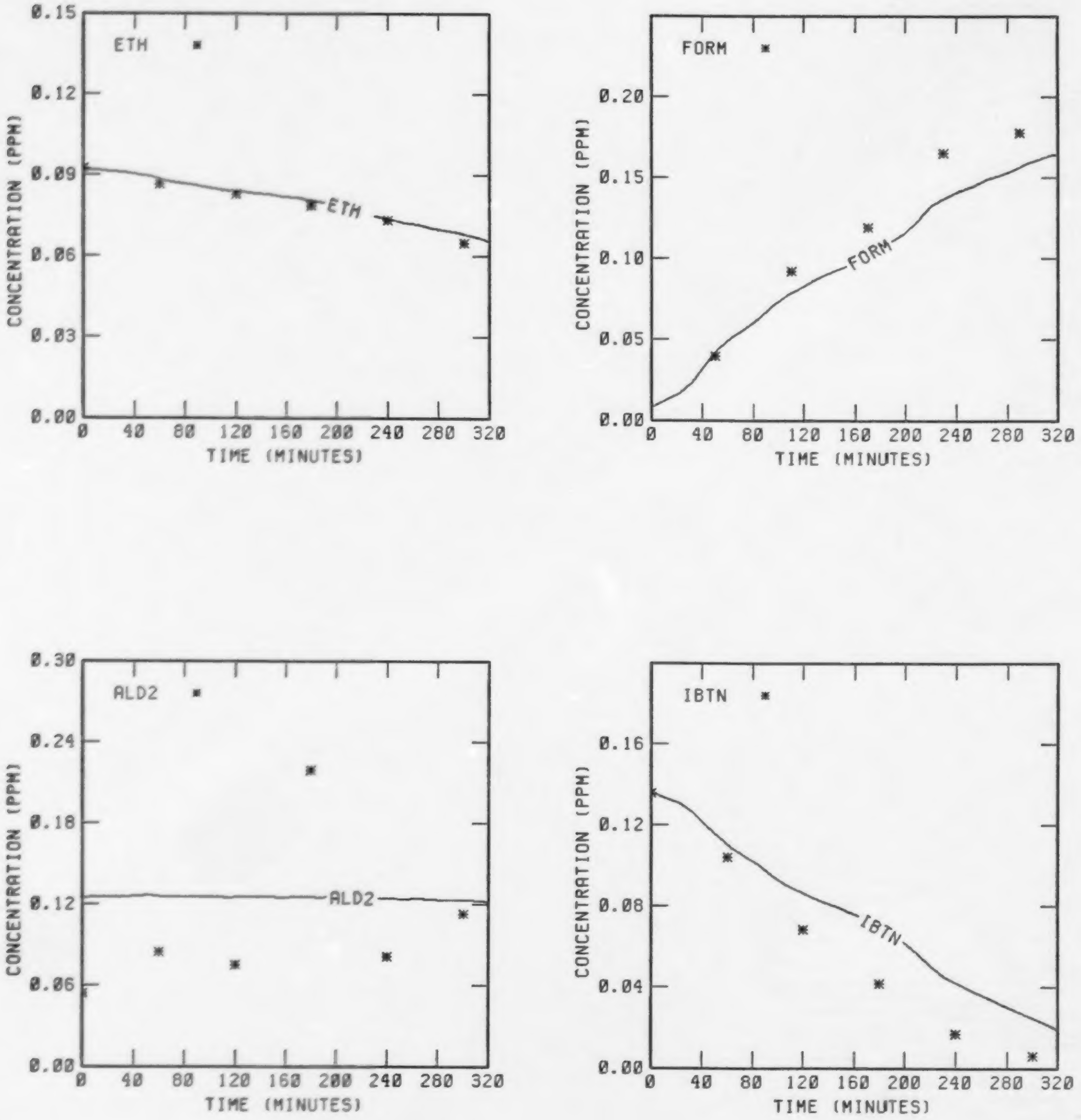


FIGURE **C-33.** SIMULATION RESULTS FOR OTCR.92883

(continued).

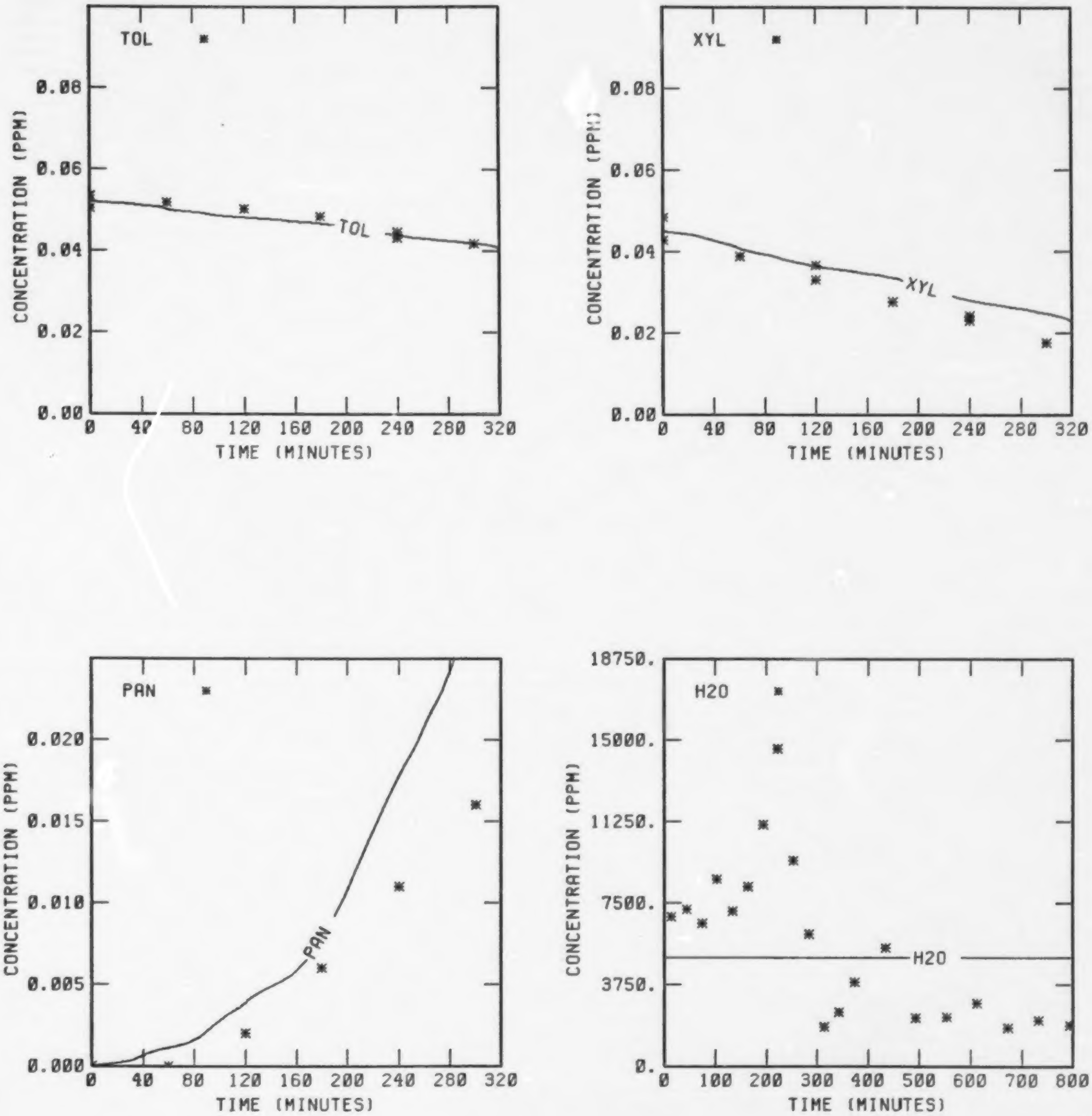


FIGURE C-33. SIMULATION RESULTS FOR
OTCR.92883

(continued).

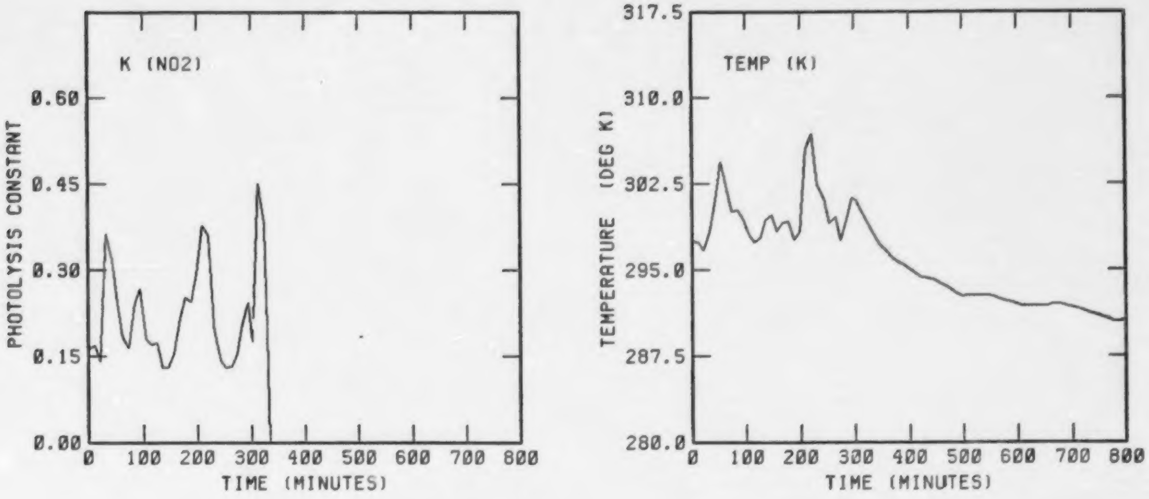


FIGURE C-33. SIMULATION RESULTS FOR
OTCR.92883

(concluded).

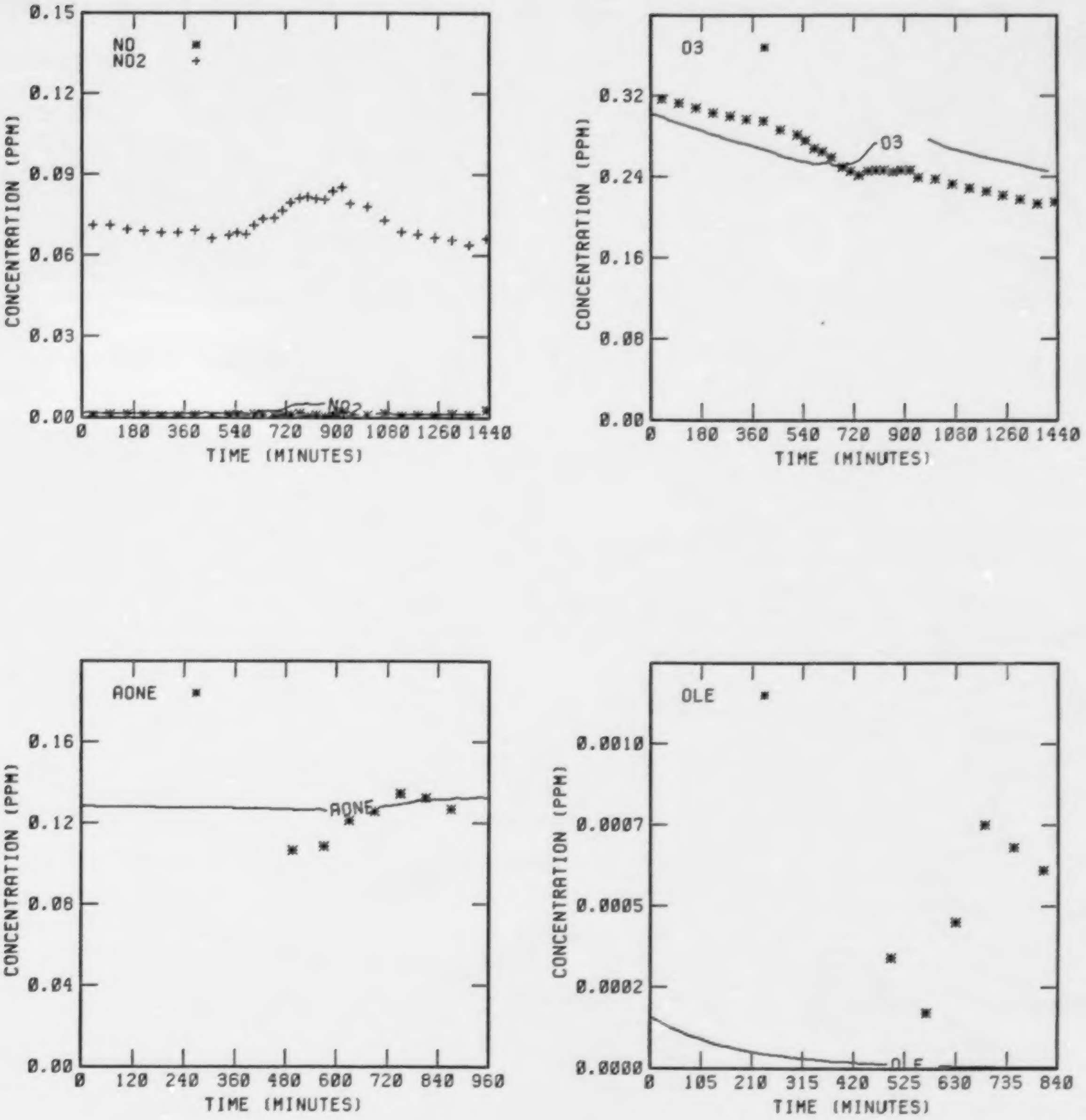


FIGURE C-34. SIMULATION RESULTS FOR
OTCB.100583

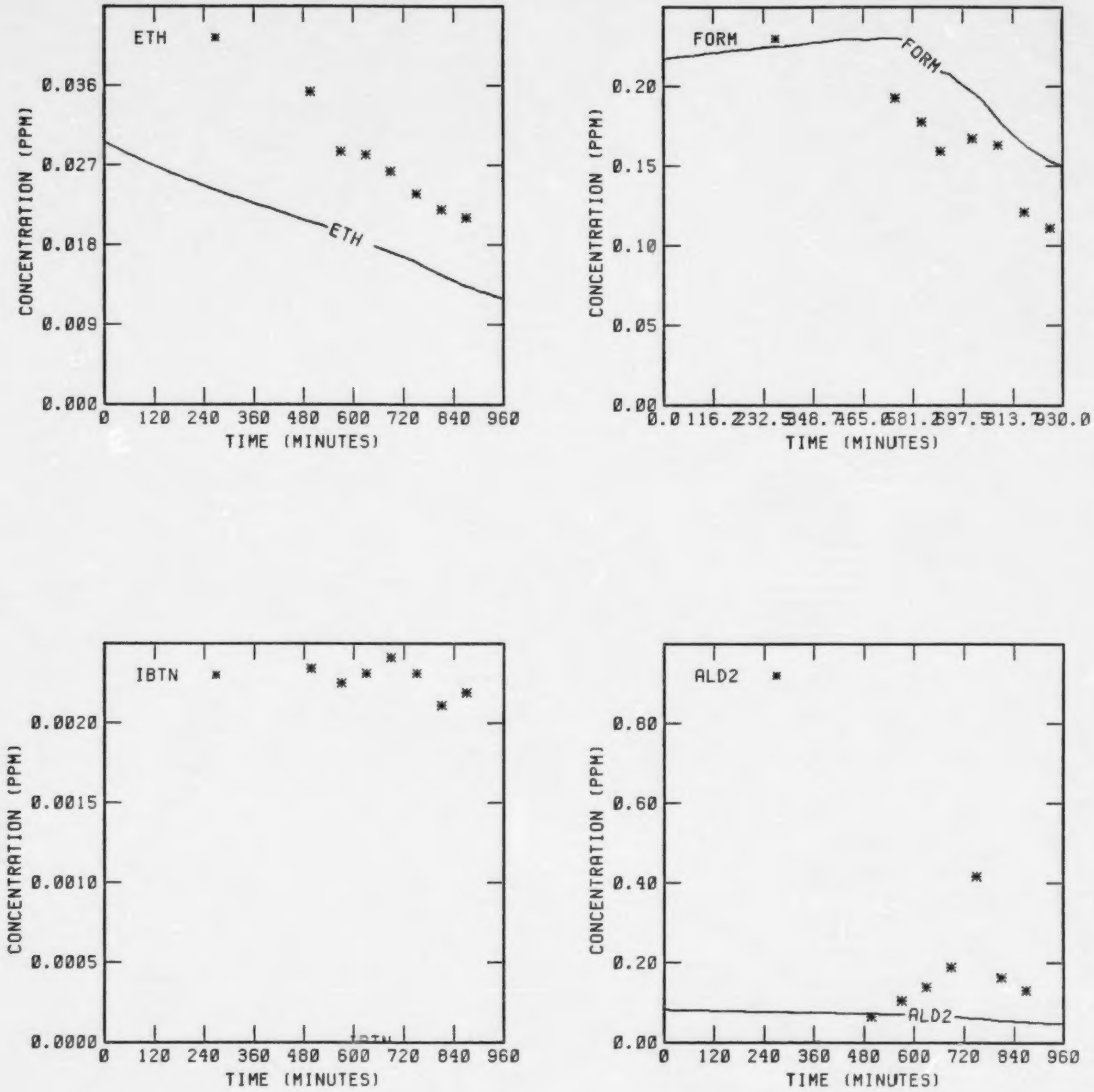


FIGURE **C-34.** SIMULATION RESULTS FOR
OTCB.100583
(continued).

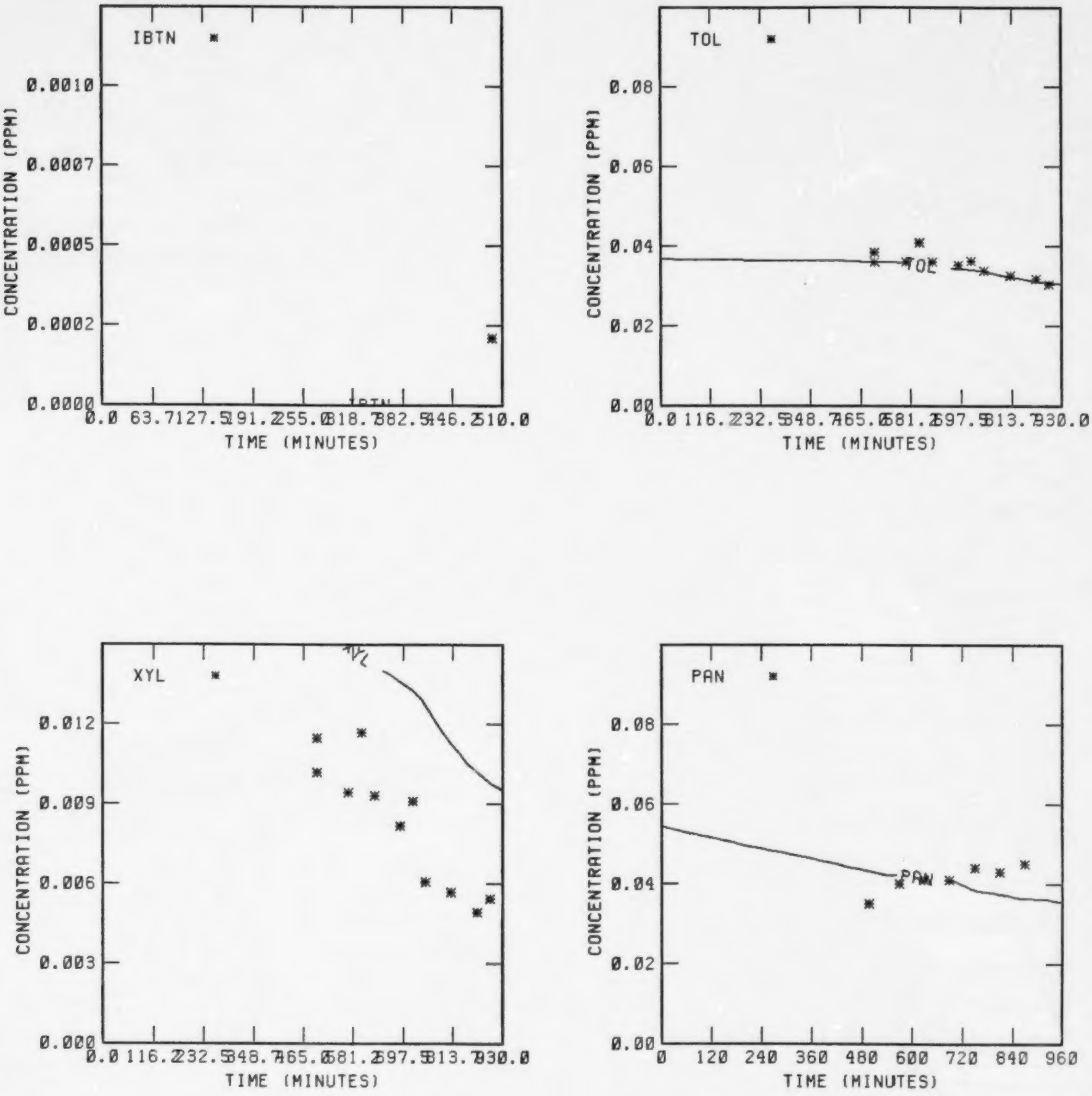


FIGURE C-34. SIMULATION RESULTS FOR
OTCB.100583
(continued).

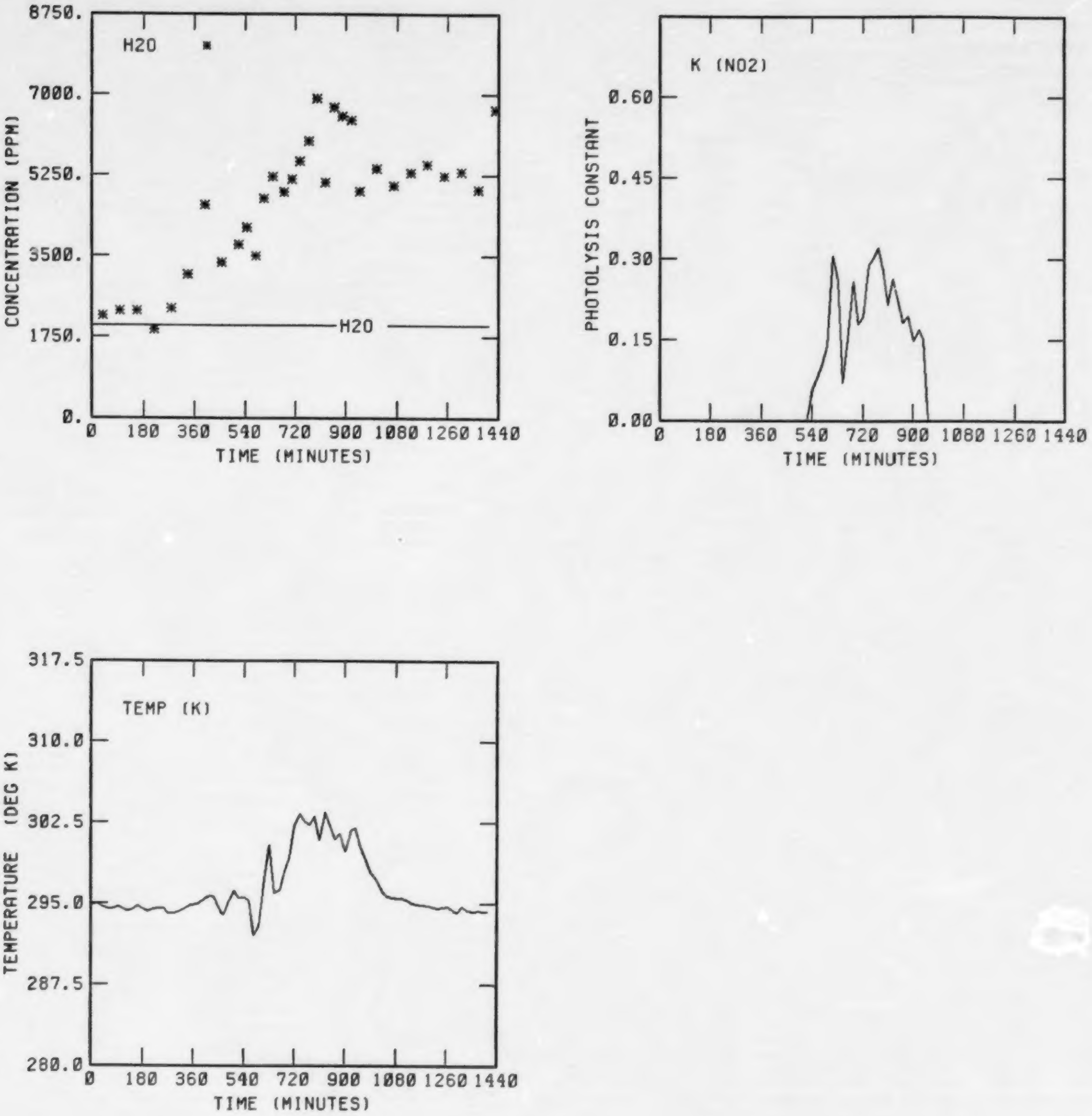


FIGURE C-34. SIMULATION RESULTS FOR OTCB.100583 (concluded).

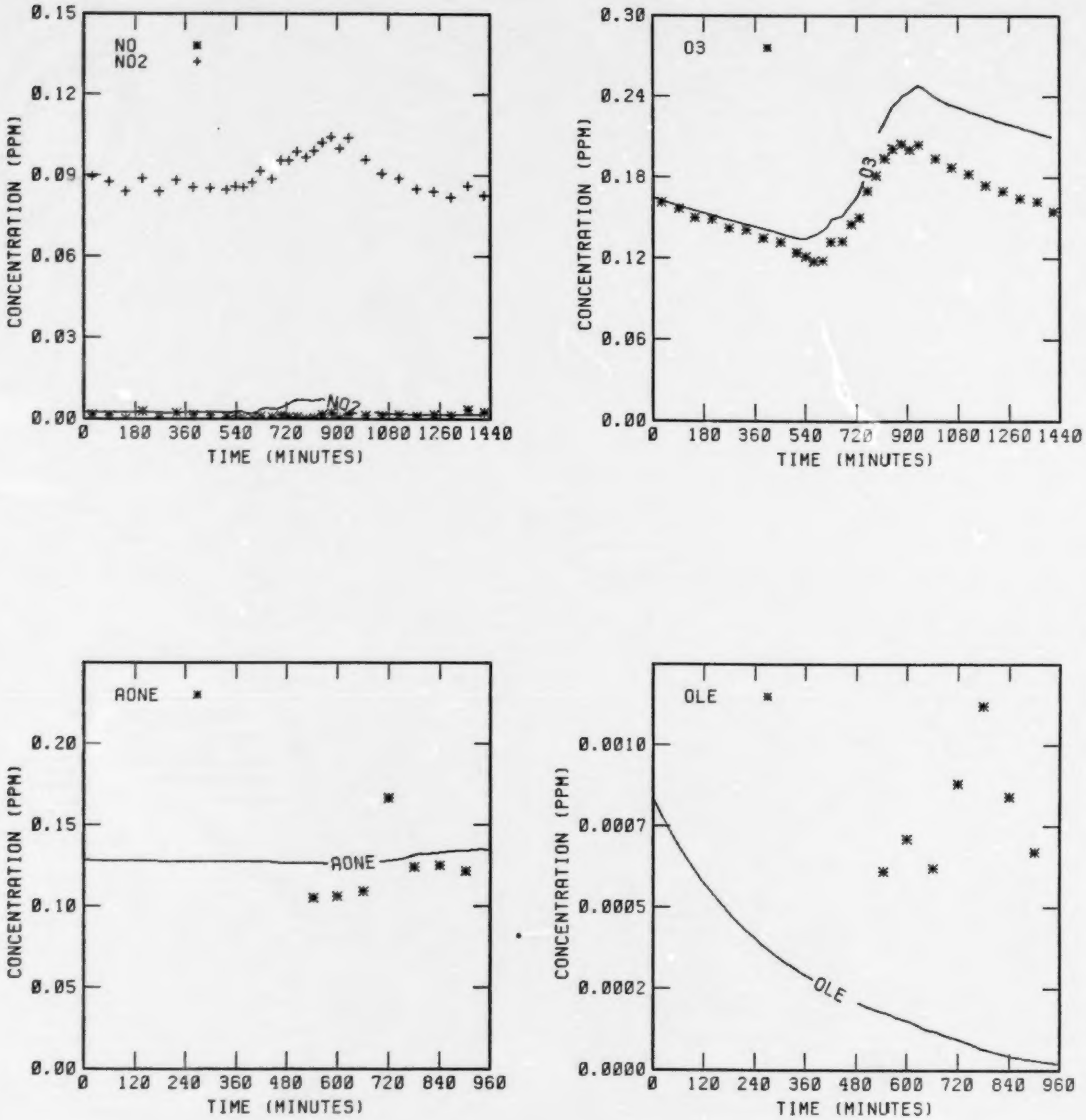


FIGURE C-35. SIMULATION RESULTS FOR
OTCR.100583

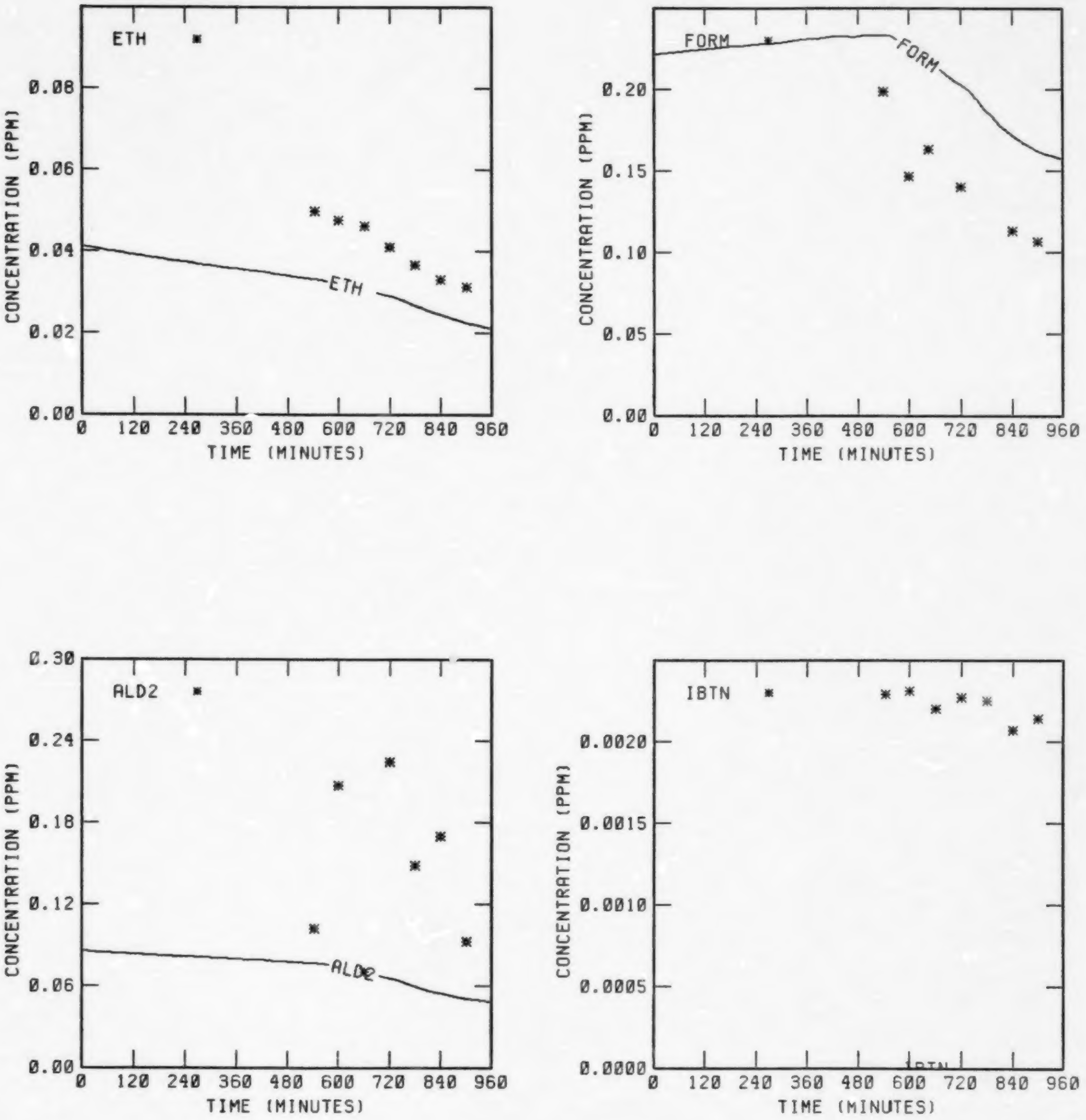


FIGURE C-35. SIMULATION RESULTS FOR
OTCR.100583

(continued).

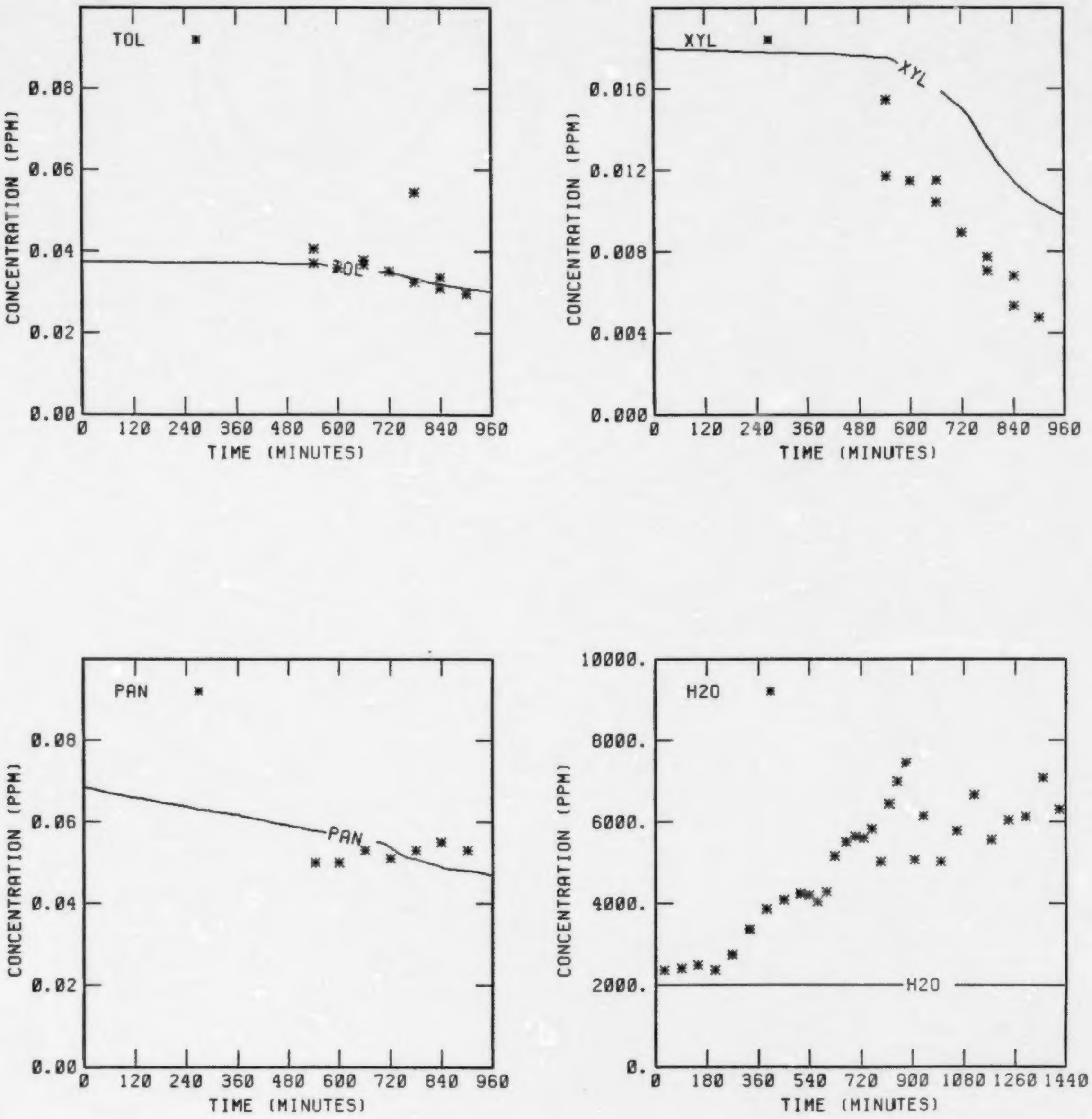


FIGURE C-35. SIMULATION RESULTS FOR
OTCR.100583
(continued).

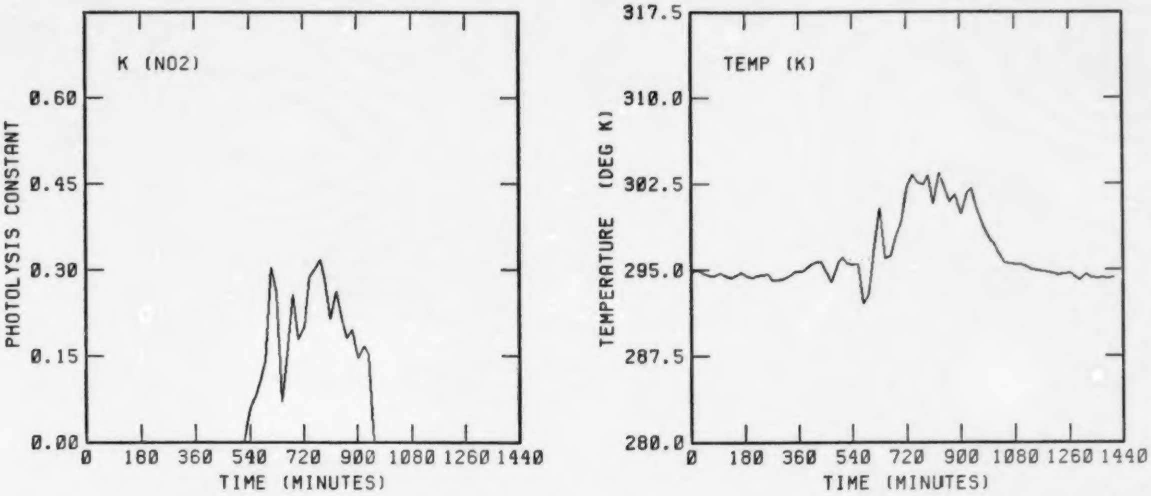


FIGURE C-35. SIMULATION RESULTS FOR
OTCR.100583
(concluded).

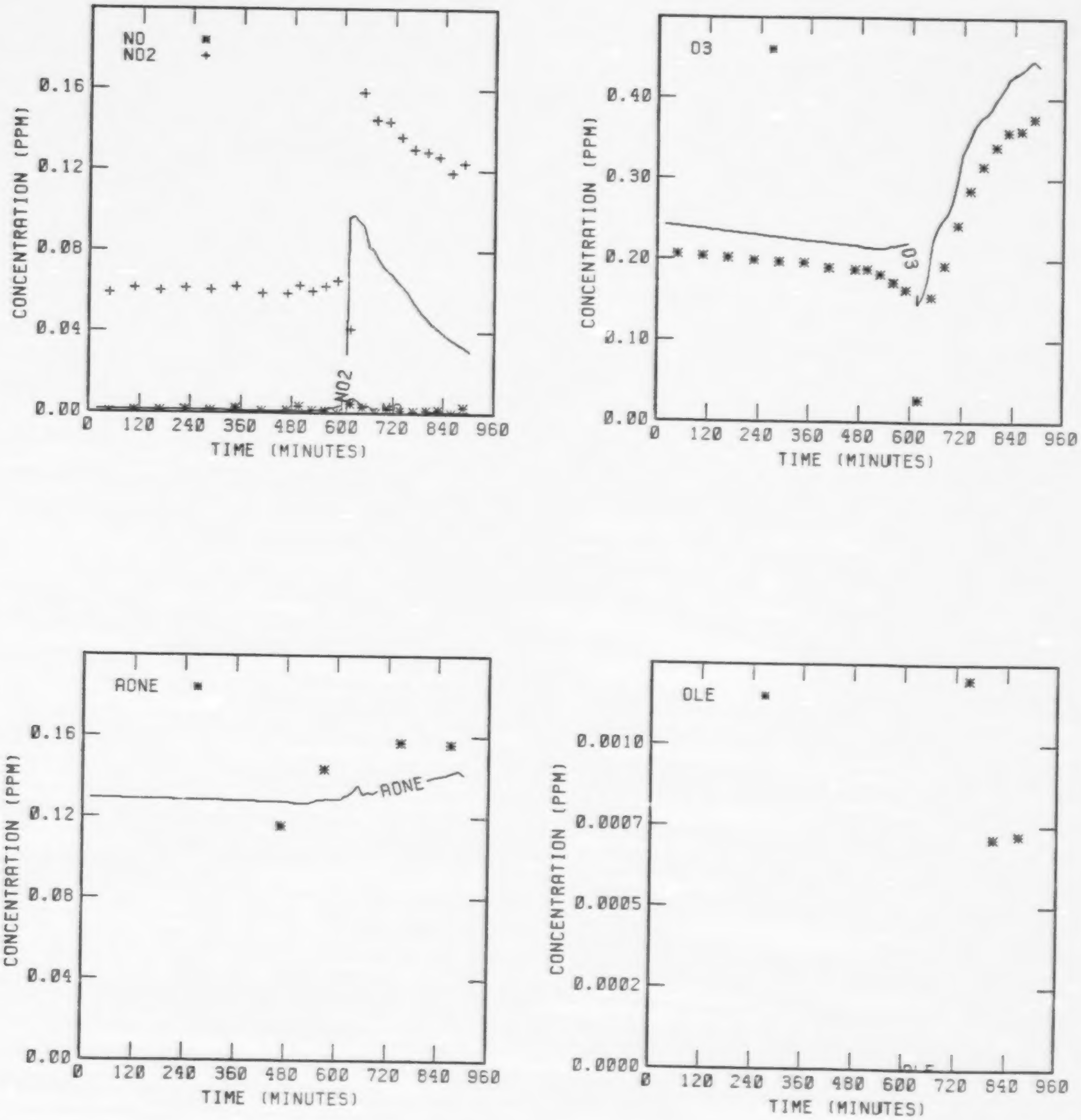


FIGURE C-36. SIMULATION RESULTS FOR
OTCB.100683

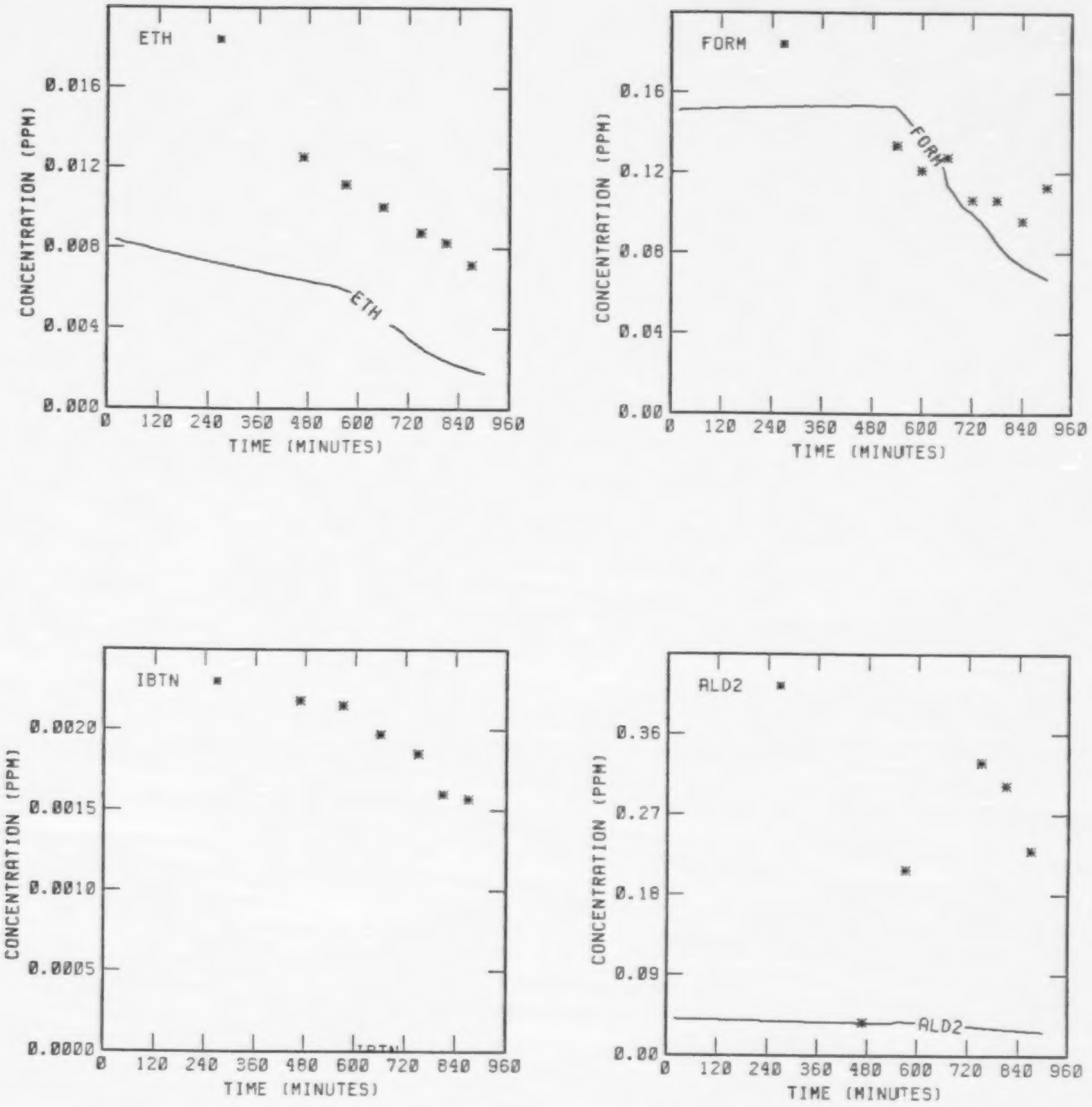


FIGURE **C-36.** SIMULATION RESULTS FOR
OTCB.100683
(continued).

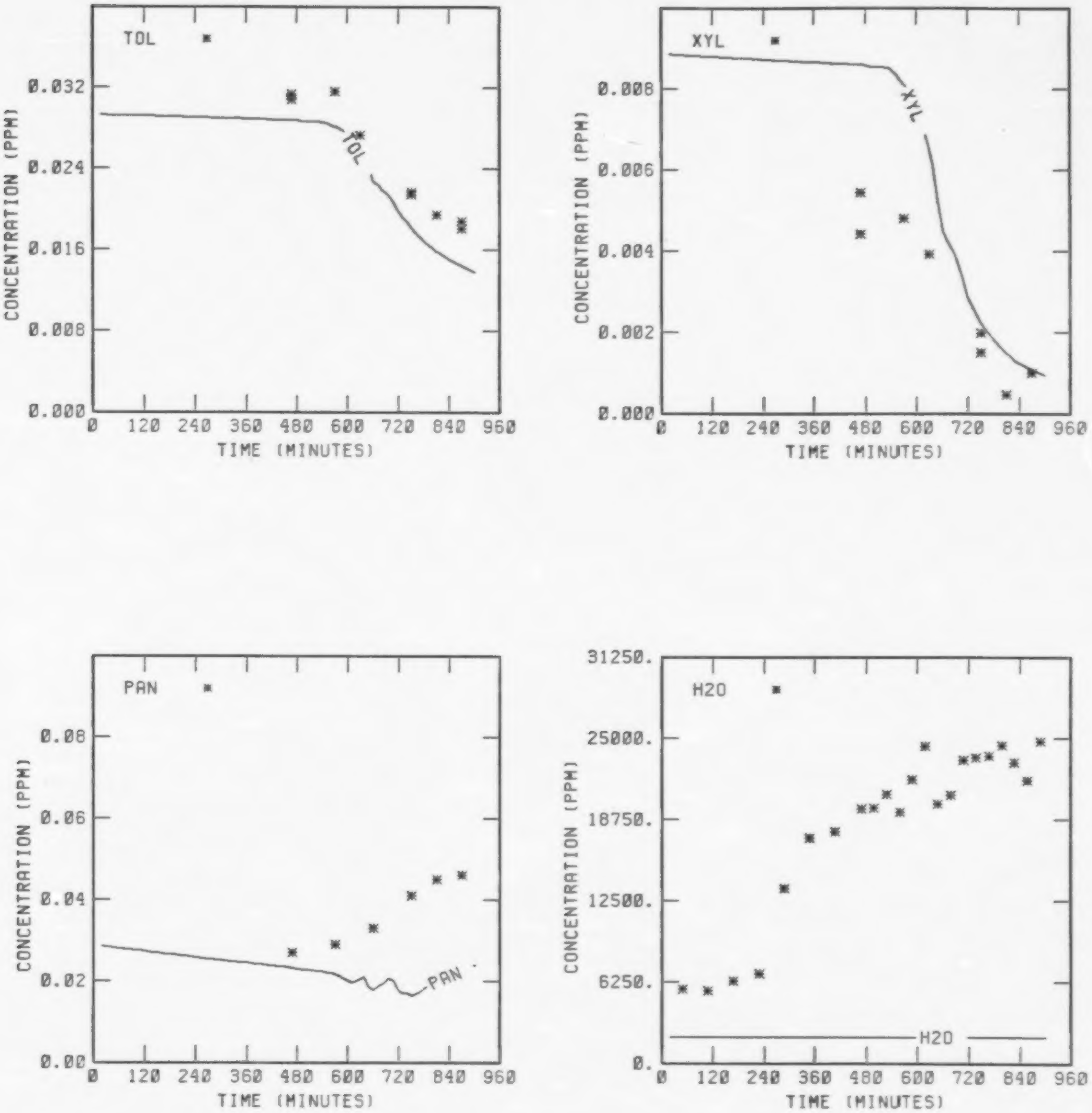


FIGURE C-36. SIMULATION RESULTS FOR
OTCB.100683
(continued).

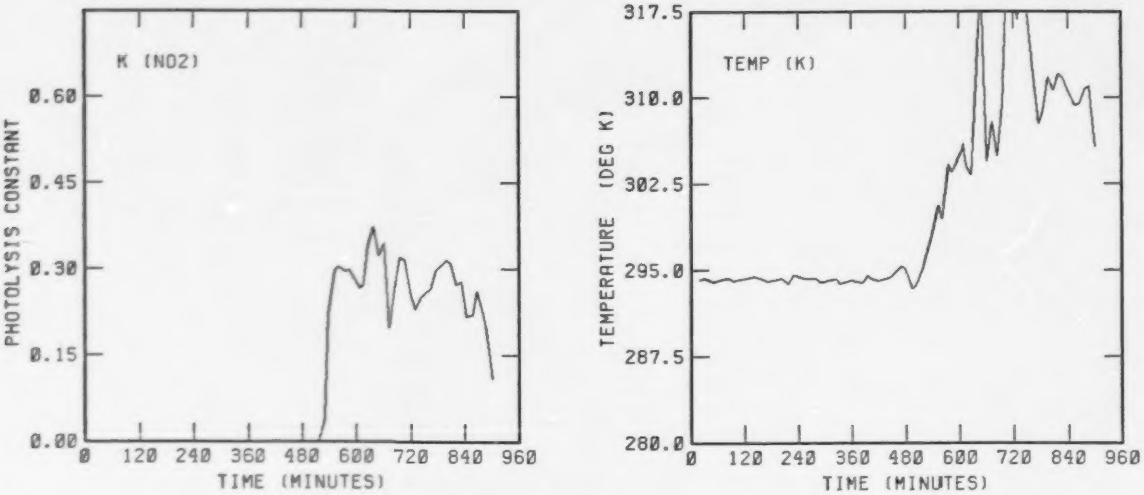


FIGURE C-36. SIMULATION RESULTS FOR OTCB.100683

(concluded).

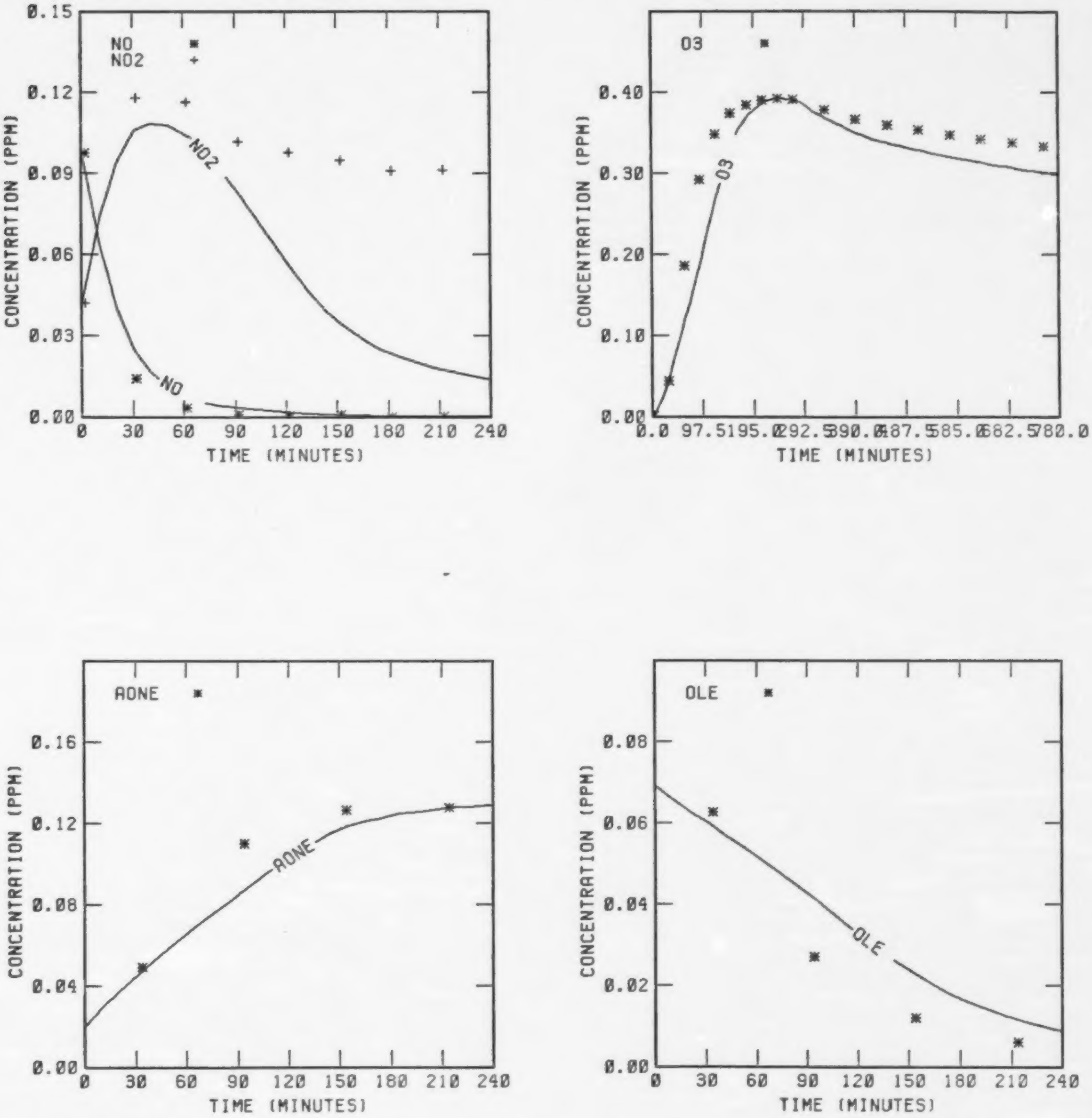


FIGURE C-37. SIMULATION RESULTS FOR
OTCB.101083

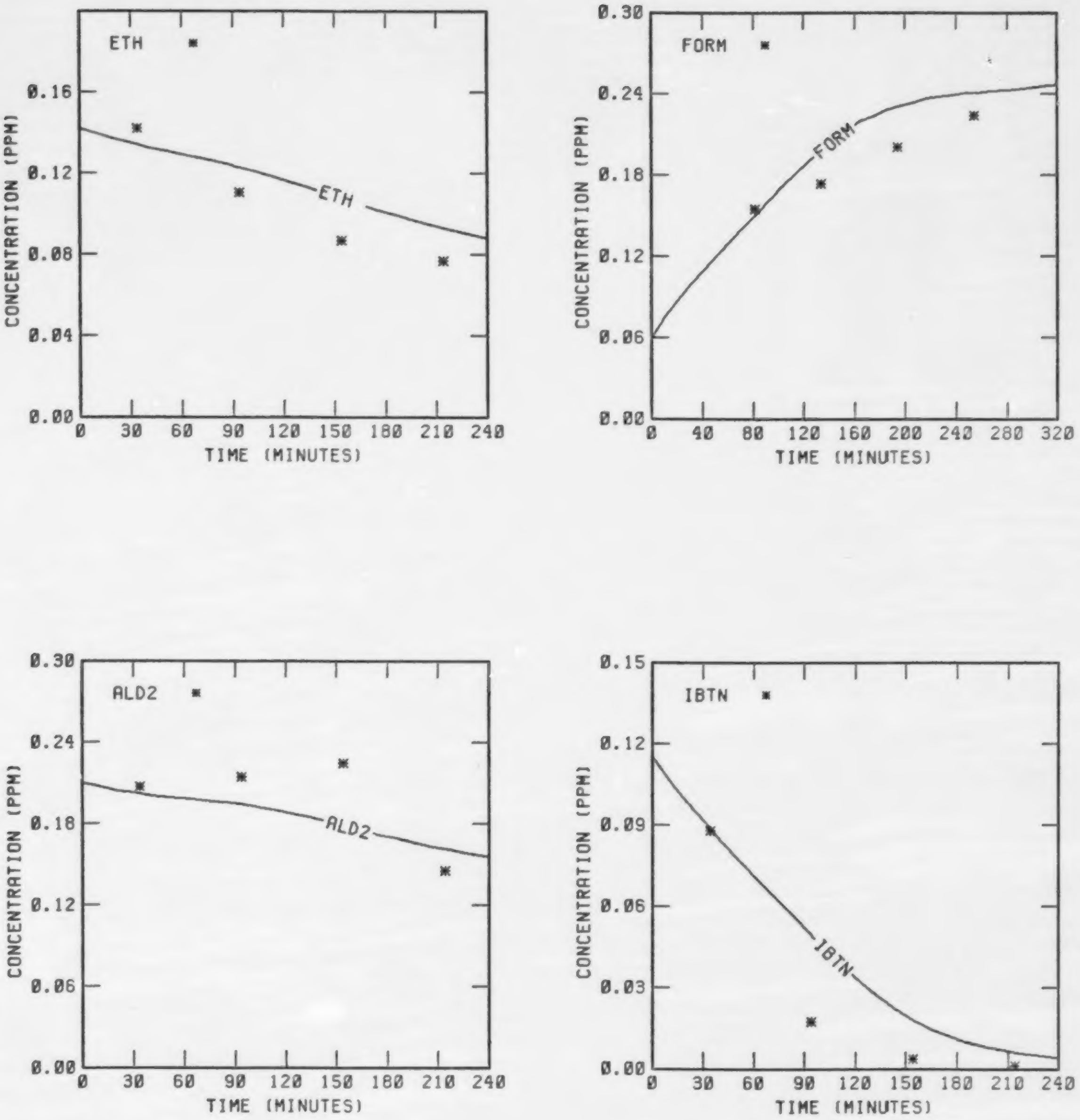


FIGURE C-37. SIMULATION RESULTS FOR
OTCB.101083

(continued).

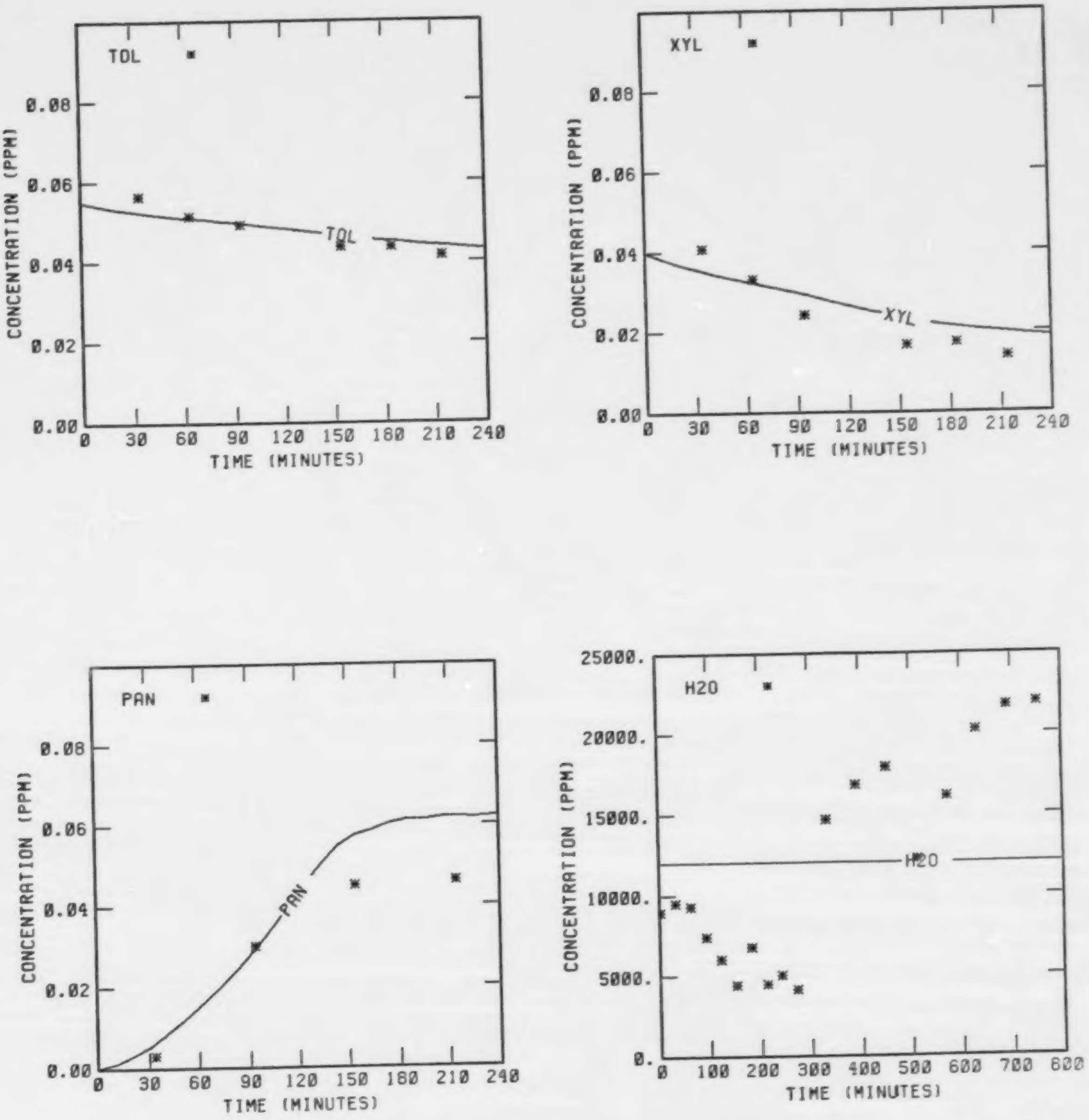
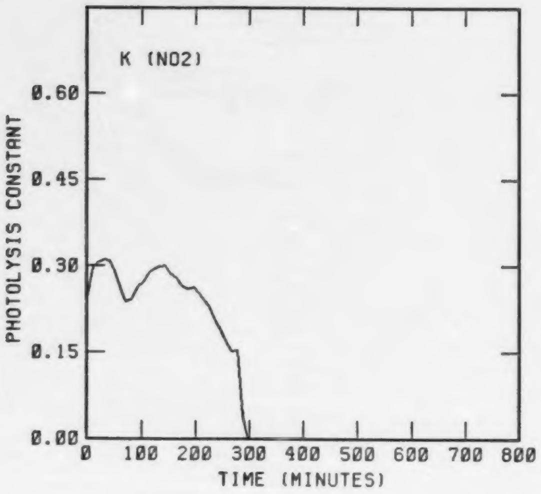


FIGURE C-37. SIMULATION RESULTS FOR OTCB.101083

(continued).



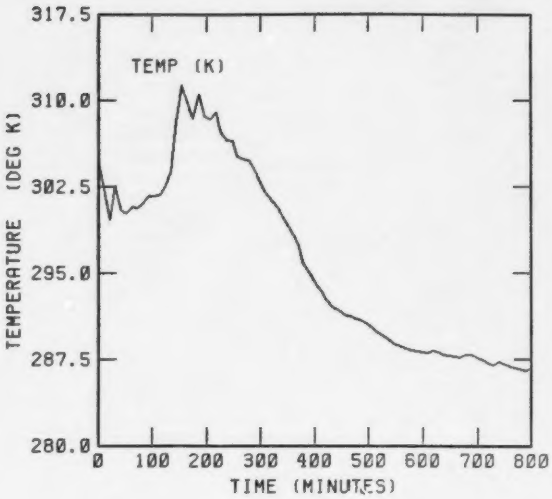


FIGURE C-37. SIMULATION RESULTS FOR
OTCB.101083

(concluded).

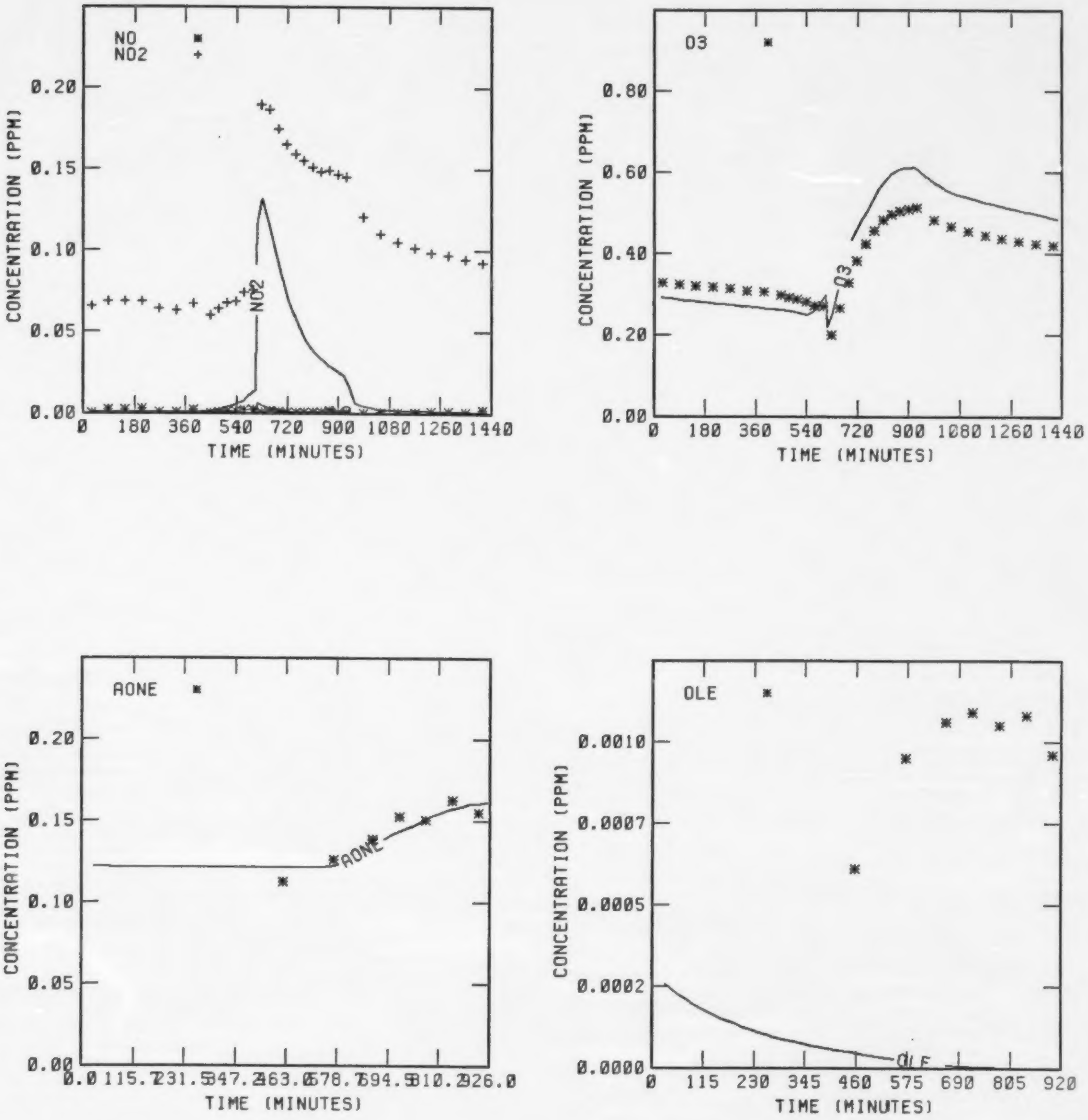


FIGURE C-38. SIMULATION RESULTS FOR
OTCB.101183

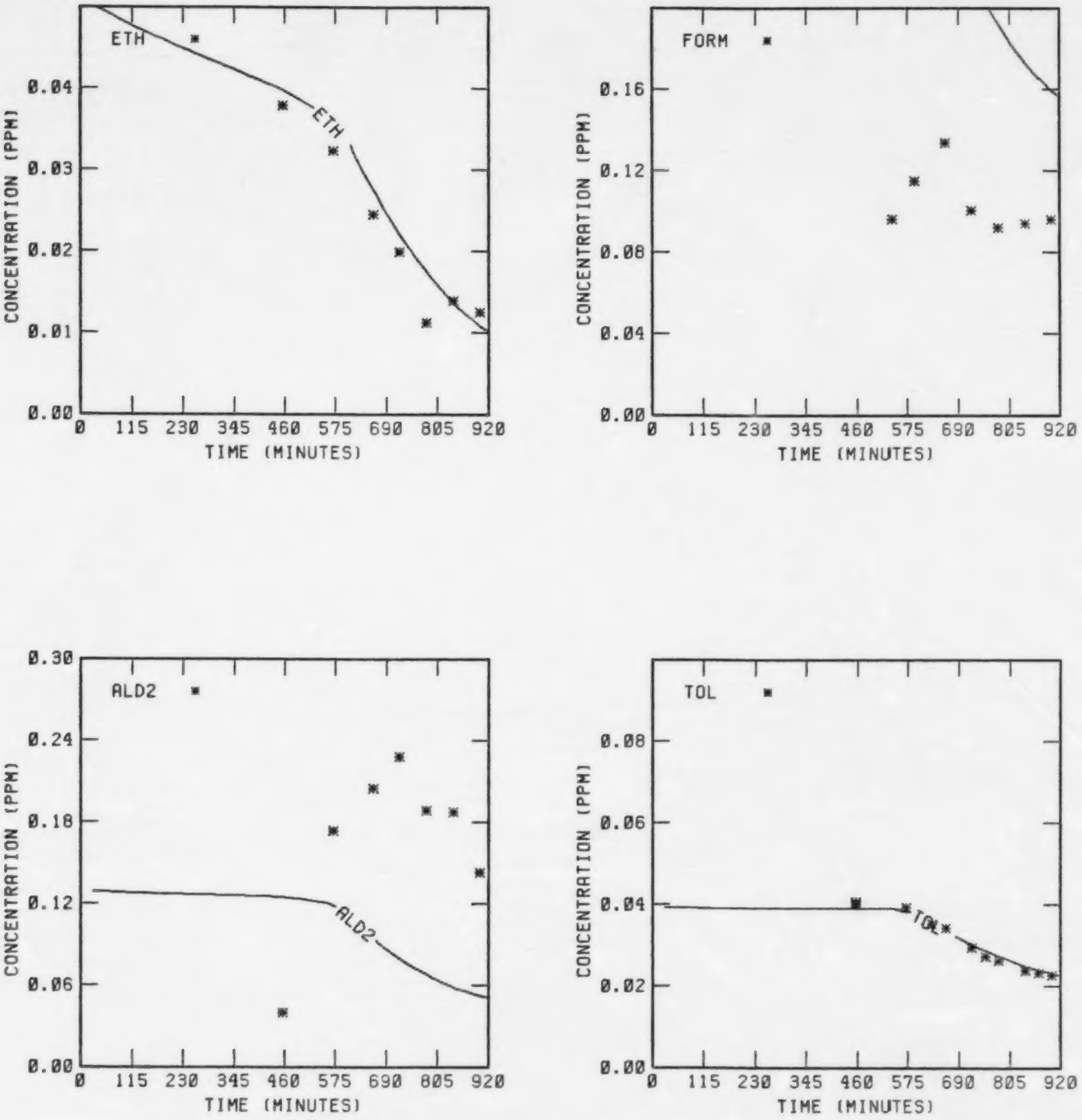


FIGURE C-38. SIMULATION RESULTS FOR
OTCB.101183
(continued).

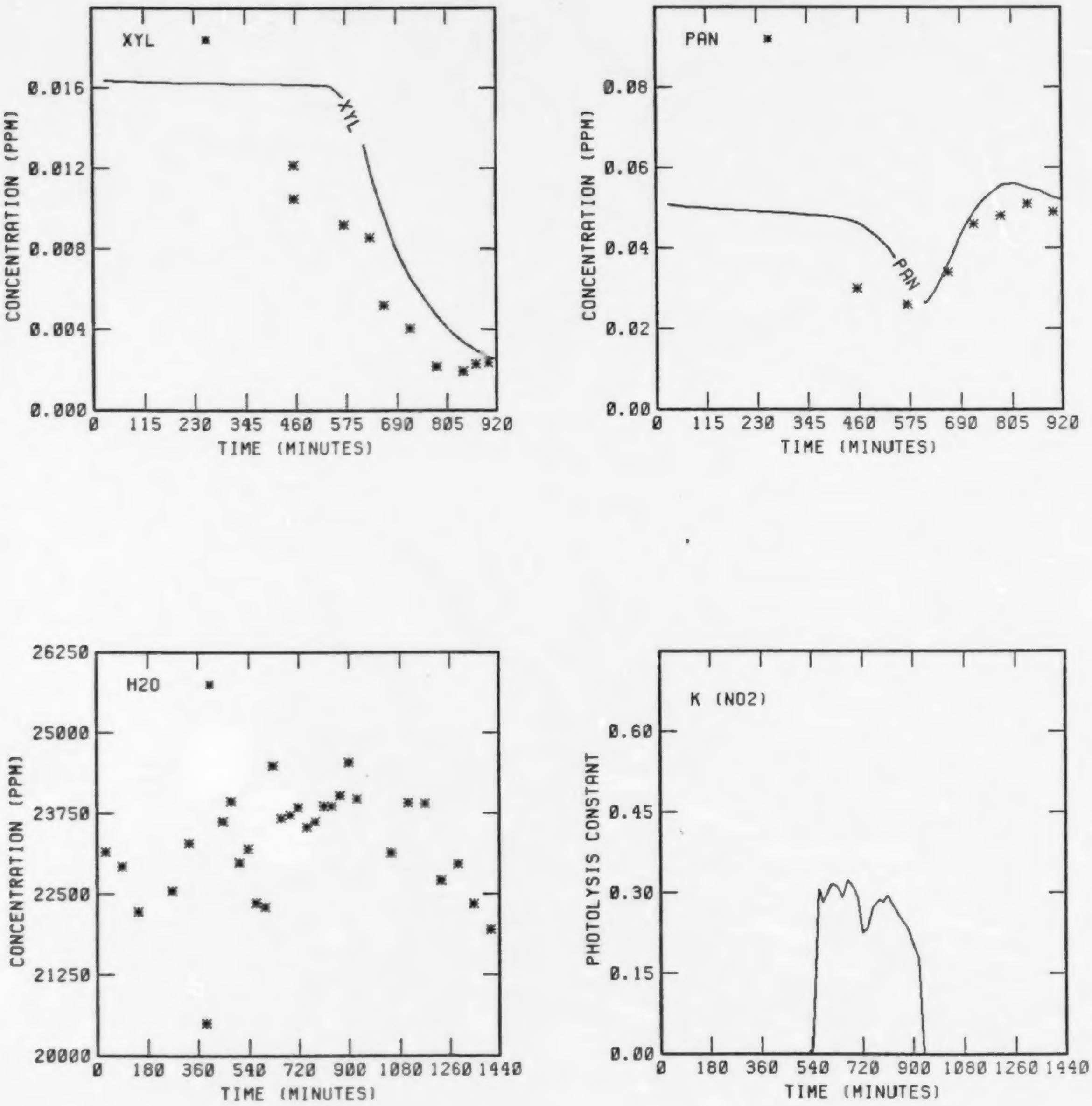


FIGURE C-38. SIMULATION RESULTS FOR
OTCB.101183
(continued).

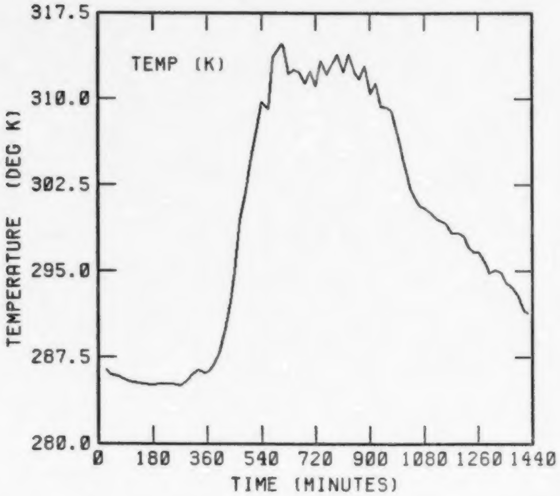


FIGURE C-38. SIMULATION RESULTS FOR OTCB.101183 (concluded).

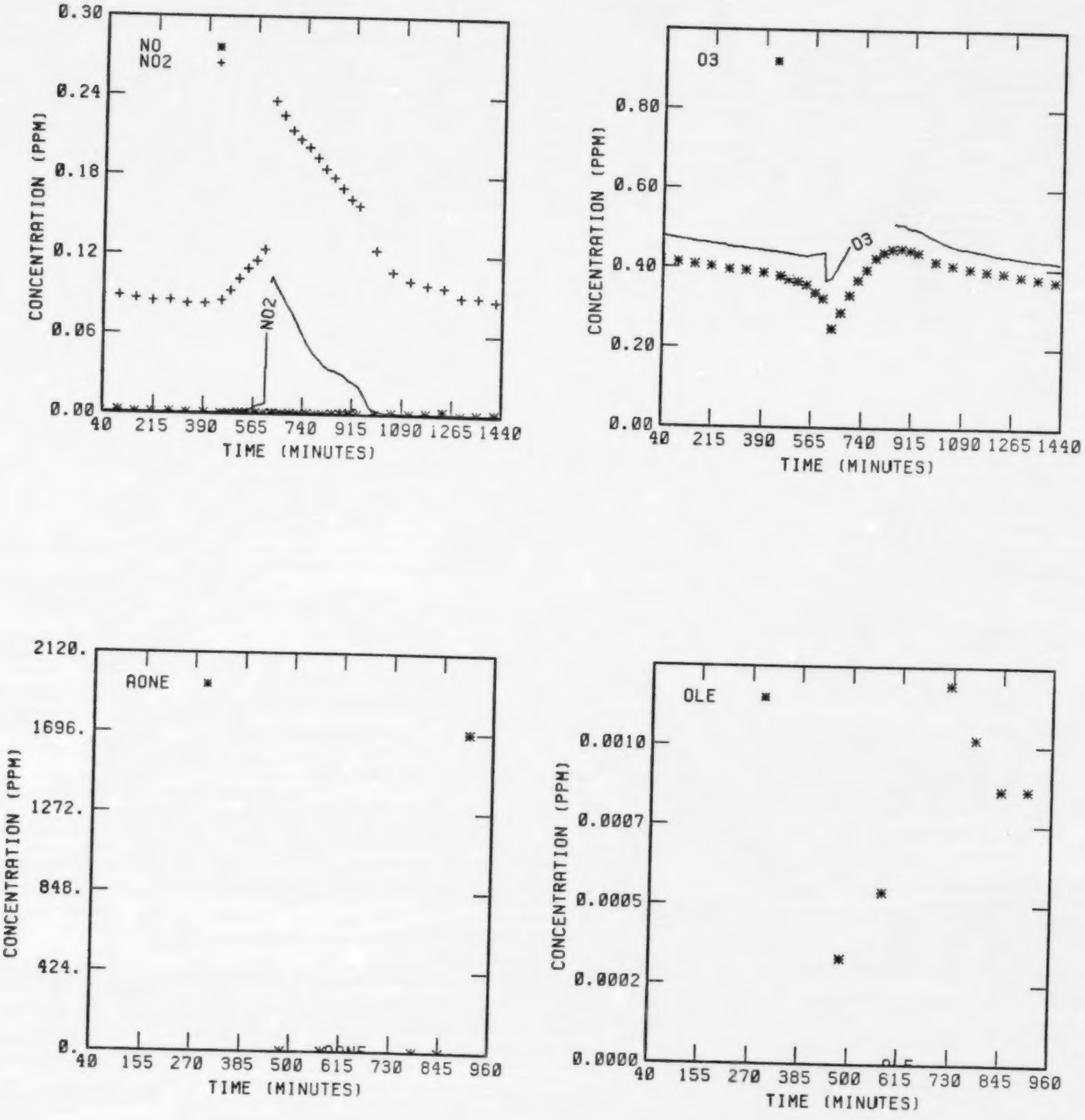


FIGURE C-39. SIMULATION RESULTS FOR
OTCB.101283

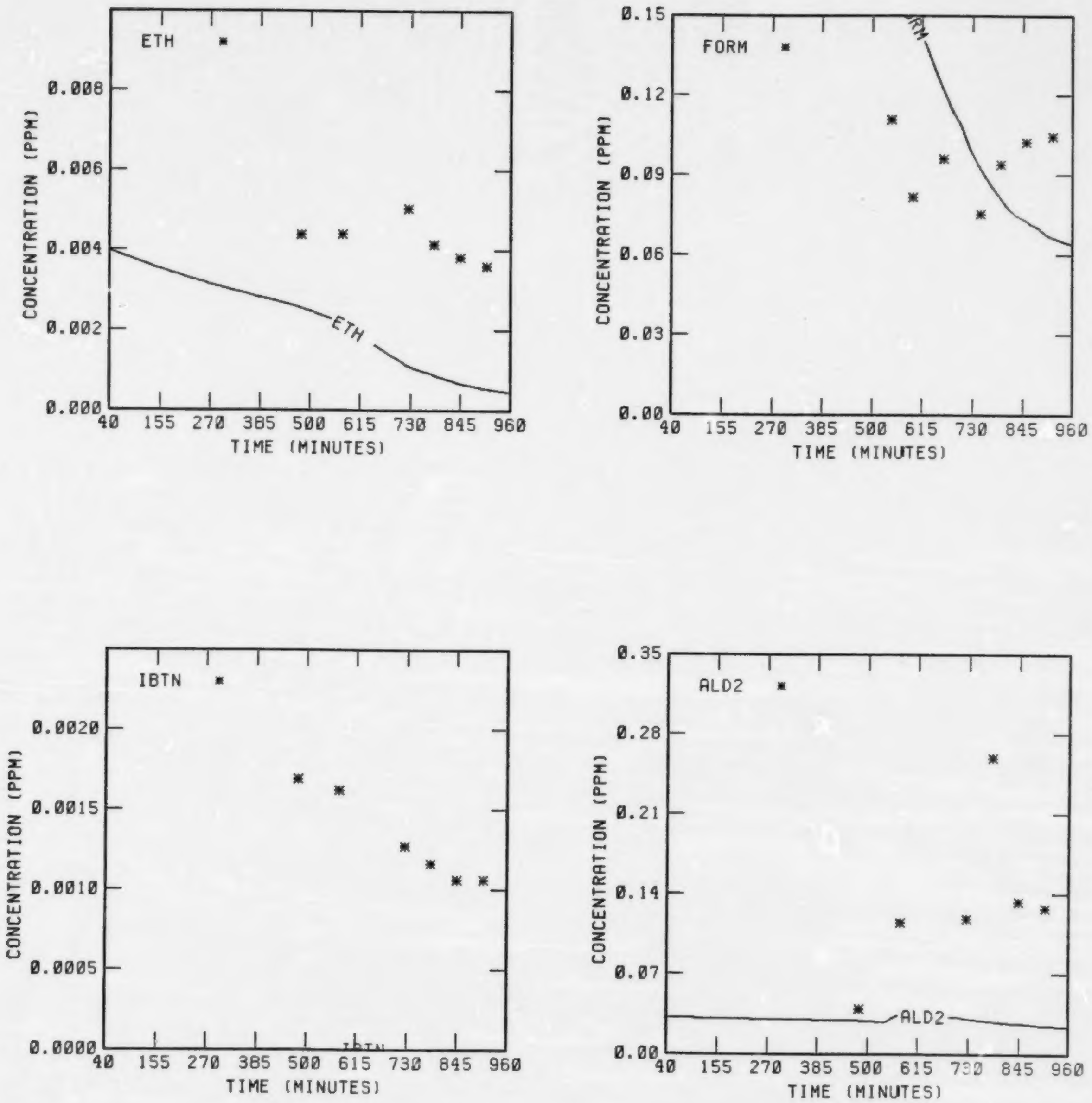


FIGURE C-39. SIMULATION RESULTS FOR
OTCB.101283
(continued).

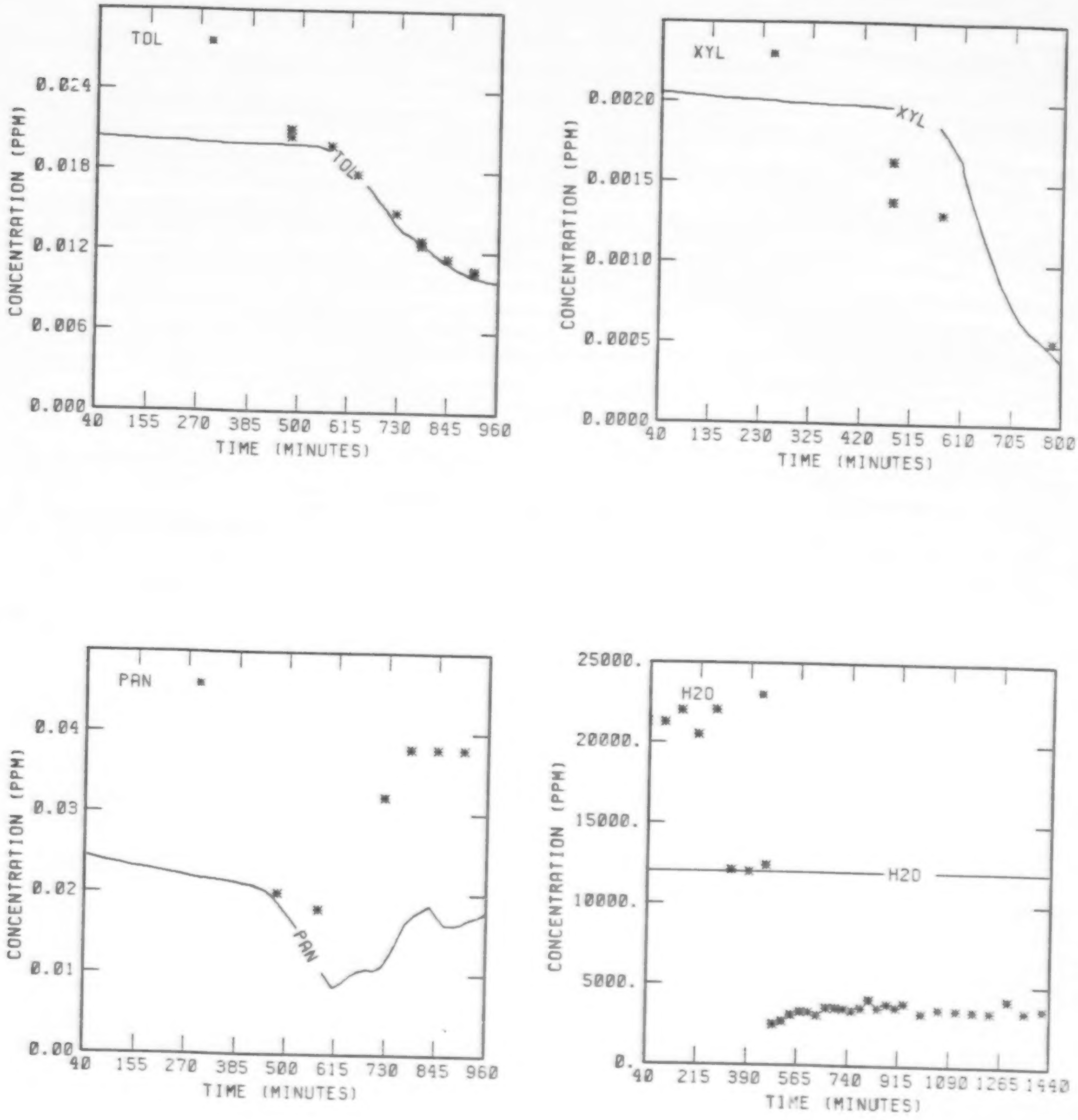


FIGURE C-39. SIMULATION RESULTS FOR
OTCB.101283

(continued).

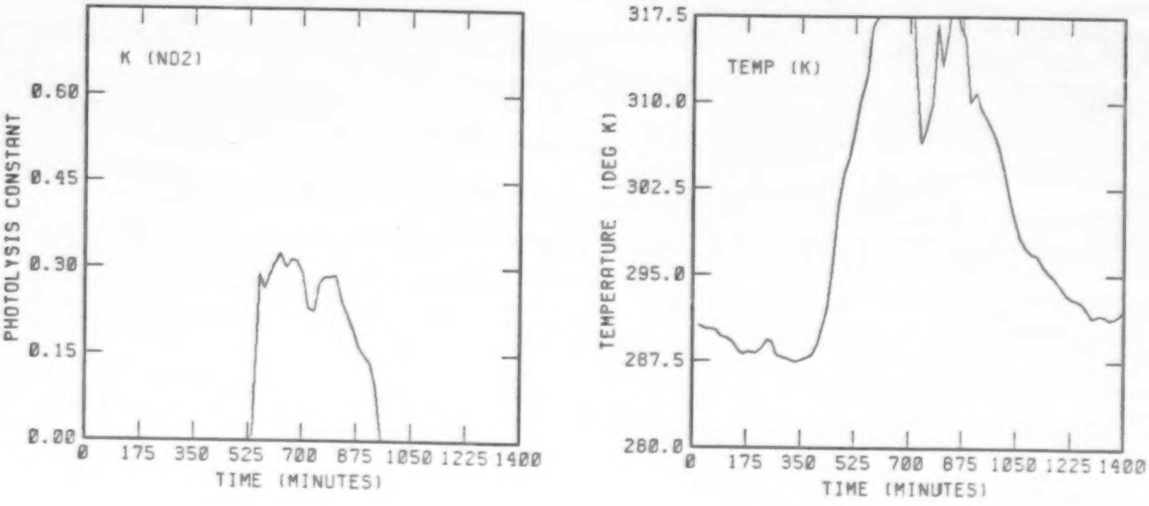


FIGURE C-39. SIMULATION RESULTS FOR
OTCB.101283
(concluded).

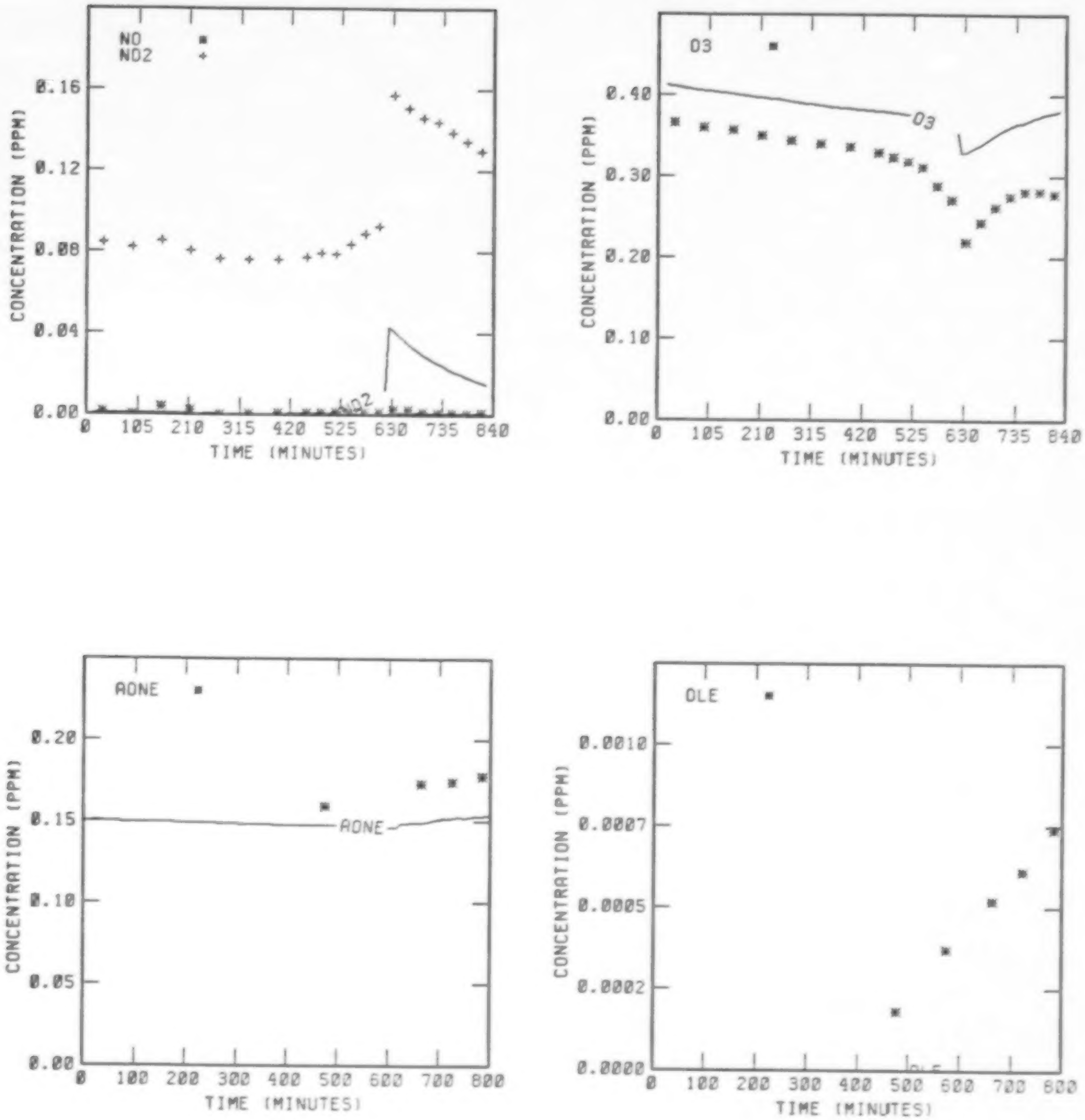


FIGURE C-40. SIMULATION RESULTS FOR
OTCB.101383

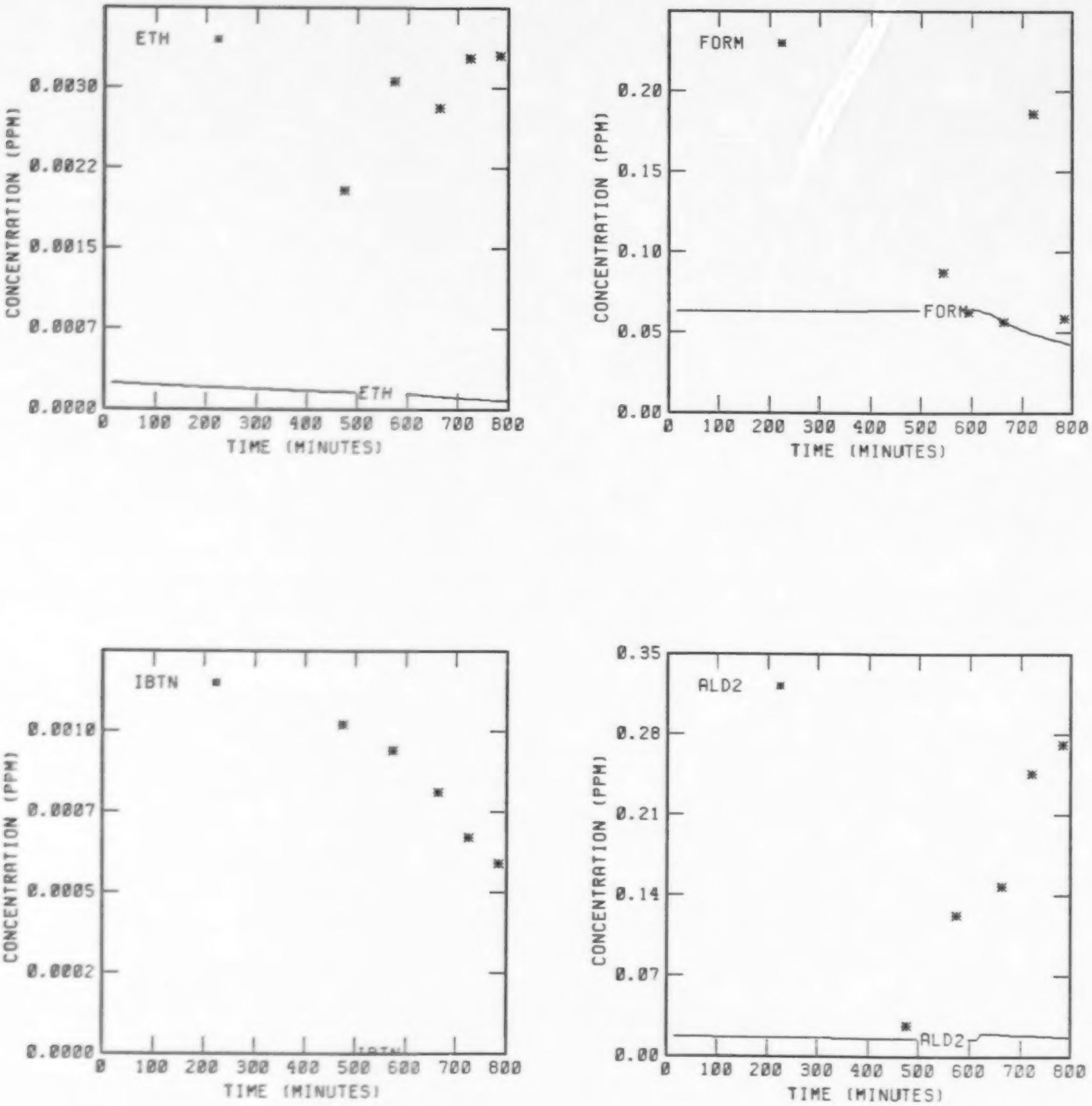


FIGURE C-40. SIMULATION RESULTS FOR
OTCB.101383

(continued).

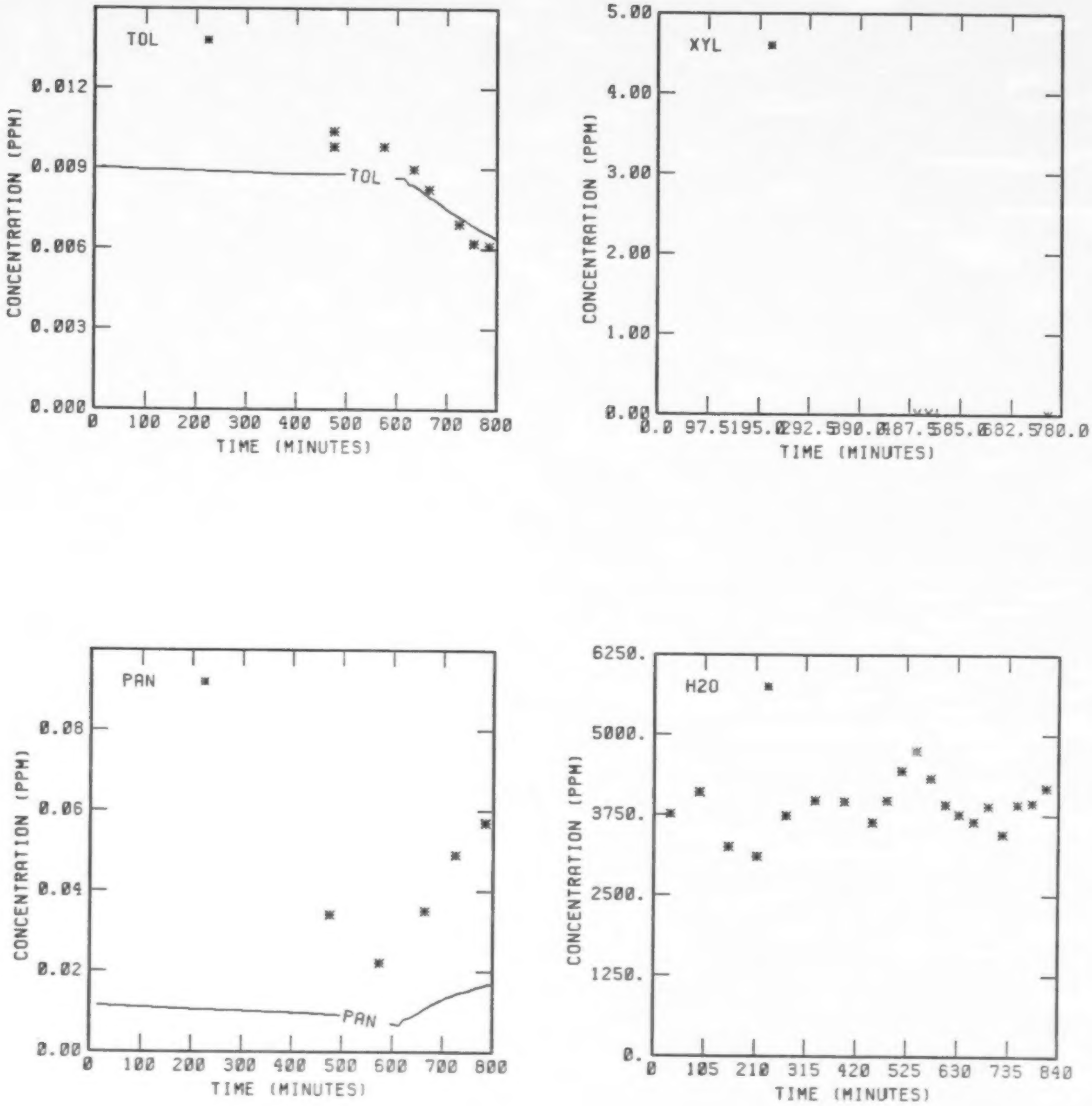


FIGURE C-40. SIMULATION RESULTS FOR
OTCB.101383

(continued).

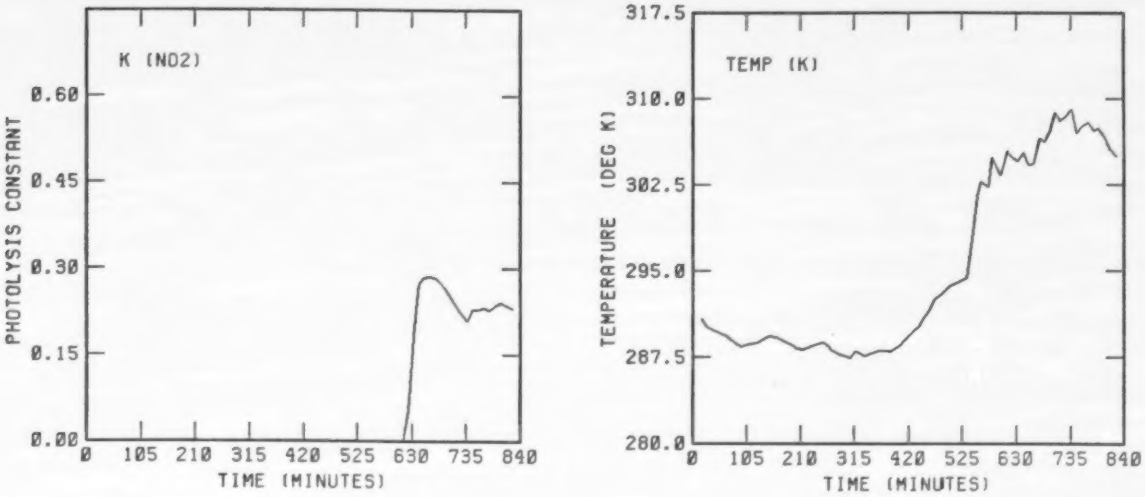


FIGURE C-40. SIMULATION RESULTS FOR
OTCB.101383
(concluded).